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U. S. DEPARTMENT OF AGRICULTURE,
FOREST SERVICE—BULLETIN 105.
HENRY S. GRAVES, Forester.

FOREST PRODUCTS LABORATORY SERIES.

WOOD TURPENTINES:

THEIR ANALYSIS, REFINING, AND COMPOSITION, BASED UPON EXPERIMENTS AT THE FOREST PRODUCTS LABORATORY AT MADISON, WIS.

BY

L. F. HAWLEY,
Chemist in Forest Products.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1913.

FOREST SERVICE.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Forest Service,
Washington, D. C., January 30, 1912.

Sir: I have the honor to transmit herewith a manuscript entitled "Wood Turpentines: Their Analysis, Refining, and Composition," by L. F. Hawley, chemist in forest products, and to recommend its publication as Bulletin 105 of the Forest Service. The investigation was carried on at the Forest Products Laboratory maintained in cooperation with the University of Wisconsin. The Yellow Pine Manufacturers' Association contributed funds toward the purchase of the refining still. The crude turpentines used in the refining experiments were obtained through cooperation with the producers. Mr. Ernest Bateman, chemist in forest products, collaborated in the development of the analytical methods and analyzed some of the products of the refining. Mr. F. E. Lichtenthaeler, formerly assistant chemist, did most of the work in connection with the installation of the refining apparatus.

Respectfully,

Henry S. Graves,
Forester.

Hon. James Wilson,
Secretary of Agriculture.

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WOOD TURPENTINES: THEIR ANALYSIS, REFINING, AND COMPOSITION.

PURPOSE OF THE STUDY.

Crude wood turpentine is one of the important products obtained by most of the chemical industries which use waste resinous wood as a raw material. Refined turpentines from these crude wood distillates have been on the market for several years, but there has been a general lack of authentic information concerning them, especially on the relations existing between methods of production, their composition, and their properties. No simple method existed for the determination of differences in their composition. Moreover, strong prejudice has developed against any product sold under the name of wood turpentine, which has never been standardized, so that there exists a large variation in the products from different plants. Also there is a marked difference in odor between most of the wood turpentines and the commonly used "gum" turpentine or "spirits," and still further this prejudice has been aided by a general lack of definite information. Naturally this has resulted in a poor market for wood turpentines, with a correspondingly slow development of the industry and incomplete utilization of the various kinds of waste wood available. It was for the purpose of improving these conditions that this investigation was undertaken.

The following results have been obtained:

(1) A simple distillation method has been developed for the examination of turpentines. From it more complete and accurate conclusions can be drawn in regard to the composition of a turpentine than could be had from former methods of equal simplicity.

(2) Methods of refining applicable to wood turpentines of a wide range in composition have been described, based on the refining of five samples of crude wood turpentine produced by as many different commercial processes.

(3) It has been shown how the composition of wood turpentines is influenced by different methods of production, by refining, and by storage, and how wood turpentines compare with gum turpentines in composition.

The next step in the investigation, the study of the relations between composition and technical value, has been begun, but it will be some time before the results are complete.

METHOD OF ANALYSIS.

It was necessary to devise a method for the examination of the crude turpentines and the volatile products obtained from them which would fulfill the following requirements:

(1) Show quantitatively the proportions of the main constituents of the material examined, especially of those constitutents which were to be separated in the refining process.

(2) Show every possible difference in composition between the various refined turpentines.

(3) Be fairly simple and rapid in operation.

No method was available which fulfilled all these conditions. The ordinary methods for the examination of turpentines apply only to the refined product (usually to gum turpentines) and are intended mainly for the detection of adulterations. The method described in Forest Service Circular 152[1] most nearly fulfills these conditions, because instead of determining the properties of the turpentine as a whole the turpentine is first fractionated by distillation with steam and the properties of the fractions are determined. By this method some idea of the proportion of the various constituents can be obtained.

After an analysis by this method, however, the composition of the turpentine could be expressed only in terms of "constituents uniform in composition" and "heavy residue" without the possibility of distinguishing between the different kinds of turpentine or of obtaining indications of the actual chemical constituents present. It was found also (see pp. — to —) that the separation of the main constituents of the turpentine by this method of distillation was so incomplete—especially in cases where comparatively large amounts of "heavy residue" were present—that the quantitative expression of the composition of the turpentine, even in such general terms as "constituents uniform in composition" and "heavy residue," was not accurate. It was necessary, therefore, to develop and adapt for use in this investigation another method for the examination of turpentines.

DESCRIPTION OF METHOD.

This new method is similar in general principles to that described in Circular 152, but it is modified in several details to make it simpler, more accurate, and more rapid.

[1] "The Analysis of Turpentine by Fractional Distillation with Steam," by W. C. Geer.

FRACTIONAL DISTILLATION.

Five hundred grams of the turpentine to be analyzed are weighed in a round-bottomed flask of about 1,000 cubic centimeter capacity; the flask is connected with a condenser by a Hempel column of the shape and size shown in figure 1, in the top of which is placed a thermometer with the bulb reaching to within 1 inch of the beads. The flask is heated on a sand bath or a piece of asbestos board and, in order to keep the liquid boiling smoothly, without bumping, a small flat coil of copper or nickeled wire is laid on the bottom of the flask. If the room temperature is very low a shield of asbestos board around the flask may also be desirable. The distillation is carried on at a maximum rate of two drops a second[1] and the distillate is caught in weighed flasks of about 100 c. c. capacity. Neither the size of the fractions—that is, the amount of distillate to be caught in each separate flask—nor the amount of undistilled residue to be left in the distilling flask can be definitely specified, since the proper amounts may vary with different kinds of turpentines. In general, however, the fractions may well be larger (10 to 12 per cent) when the temperature of the distillation is changing slowly and regularly, but should be smaller (4 to 5 per cent) when the temperature is changing rapidly. Usually, also, it is unnecessary to continue the distillation after a temperature of 180° C. (corrected) is reached, because this seems to be the temperature below which almost all of the turpentine materials are distilled over and above which the heavy oils begin to come over in large quantities. This is especially true in the case of wood turpentines. With gum turpentines and some wood turpentines, however, especially those with a small amount of heavy oil, the turpentine materials are all distilled over before this temperature is attained.

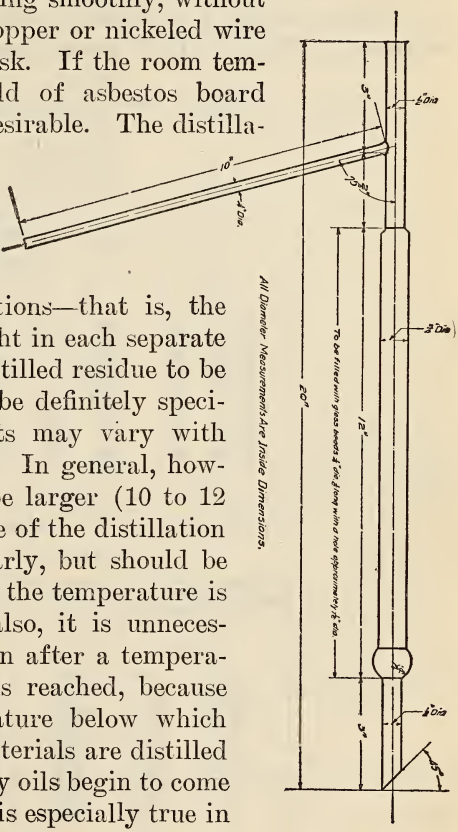

FIG. 1.—Hempel column.

There are many details of manipulation which can not be completely specified in a method which is to be applied to materials of

[1] A slower distillation gives, of course, a better fractionation, and the maximum rate mentioned should never be exceeded; there should, moreover, be no tendency to hasten the distillation in order to save time, because the work of determining the amount and properties of the fractions can be carried out at the same time as the distillation. Indeed, a moderately rapid and experienced worker, with all the apparatus handy, can make the necessary determinations and computations, and can record and plot the results on six or seven fractions, while nine or ten are being distilled.

widely variable character. However, ordinary intelligence and a little experience are sufficient to indicate the proper variations in detail.

EXAMINATION OF FRACTIONS.

The weight of each fraction is determined and the percentage weights of each fraction and of the total combined fractions (see Table 1) are then computed. The maximum boiling point of each fraction is read from the thermometer at the top of the column, and the specific gravity and index of refraction of each fraction and of the residue left in the flask are determined.

TABLE 1.—*Typical data sheet showing records of distillations.*

Fraction No.	Temperature.						Weight.		
	T.	*t.*	*T*−*t.*	*N.*	Corrected barometer, 741.5 mm.	Corrected barometer, 760 mm.	Flask plus distillate.	Flask.	Distillate.
							grams.	*grams.*	*grams.*
1	156.5	49	108	56	157.4	158.5	79.6	32.1	47.5
2	157.0	50	107	57	157.9	159.0	94.1	39.0	55.1
3	157.3	50	107	57	158.2	159.3	80.3	25.3	55.0
4	157.7	51	107	57	158.6	159.7	97.6	36.6	61.0
5	158.0	50	108	58	158.9	160.0	83.1	28.3	54.8
6	158.8	50	109	58	159.7	160.8	96.7	32.5	64.2
7	159.7	51	109	59	160.6	161.7	77.4	27.3	50.1
8	162.4	51	111	62	163.4	164.5	96.2	43.5	52.7
9	167.3	52	115	67	168.4	169.5	61.0	27.1	33.9
Residue							150.6	125.5	25.1

Fraction No.	Percentage weight.		Specific gravity.			Index of refraction.		
	Single fractions.	Total combined fractions.	Determined.	Temperature.	Calculated for 15° C.	Determined.	Temperature.	Calculated for 15° C.
				°C.			°C.	
1	9.5	9.5	0.8596	21.5	0.8650	1.4693	19.5	1.4714
2	11.0	20.5	.8597	21.5	.8651	1.4694	19.5	1.4715
3	11.0	31.5	.8599	21.5	.8653	1.4695	19.5	1.4716
4	12.2	43.7	.8601	21.5	.8655	1.4699	19.5	1.4720
5	11.0	54.7	.8605	21.2	.8656	1.4702	19.5	1.4723
6	12.8	67.5	.8609	21.2	.8660	1.4707	19.2	1.4727
7	10.0	77.5	.8615	21.0	.8665	1.4714	19.2	1.4734
8	10.5	88.0	.8625	21.0	.8675	1.4730	19.2	1.4750
9	6.8	94.8	.8639	21.0	.8689	1.4760	19.2	1.4780
Residue	5.0	99.8	.9408	20.0	.9450	1.4914	21.1	1.4943

Boiling point.—The boiling temperatures as read should be corrected (1) for the prevailing barometric pressure, using the factor 0.056° for every millimeter difference from the normal, 760 mm., and (2) for the emergent stem of the thermometer according to the following formula:[1] To the observed value of the boiling point, T, should be added the factor 0.000143 $(T-t)$ N, in which t is the temperature of the thermometer stem above the cork and N the length expressed in degrees of the mercury column above the cork.

[1] Young's "Fractional Distillation," p. 12.

Specific gravity.—The specific gravity can be determined accurately enough by means of a Westphal balance, making the determinations at room temperature and correcting to 15° C. by using the factor 0.00083 for every degree centigrade of difference from this standard temperature. The correction for temperature is large enough so that especial care must be taken to make the temperature readings accurate. In order to make specific gravity determinations with the Westphal balance on as small a fraction as is often desirable, it is necessary to have a smaller cell than that usually furnished with the instrument. This can readily be made by properly shortening a test tube with a diameter only slightly greater than the bob of the balance and supporting it in a flat cork. In this way the gravity of a fraction of only 18 grams (3.6 per cent) can readily be determined on a balance with a bob having a displacement of 5 c. c.

Index of refraction.—The index of refraction can be determined with sufficient accuracy by means of an Abbé refractometer, taking the readings at room temperature and correcting by means of the factor 0.00047 for every degree difference from the standard temperature of 15° C. It has been found that this factor 0.00047 is more nearly correct for the general run of turpentines than 0.00049 (as recommended in Circular No. 152) and that the use of different temperature correction factors for different values of the index of refraction is not necessary in order to obtain the degree of accuracy required for the work.

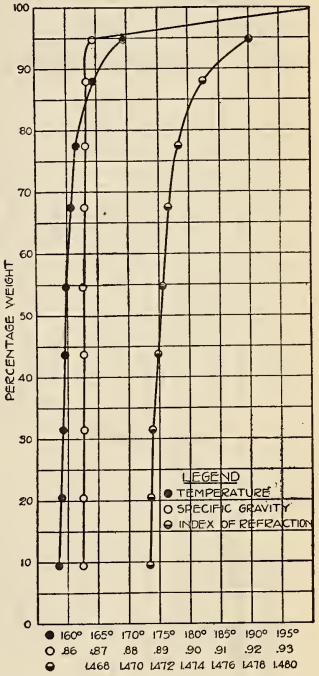

FIG. 2.—Typical curves showing boiling points, specific gravities, and indices of refraction of a gum turpentine.

RECORDING DATA.

A typical data sheet showing the original and corrected values as first recorded is shown in Table 1. For the purpose of making the interpretation of these results simpler and easier the final corrected values for the boiling point, specific gravity, and index of refraction of the different fractions are plotted against the total percentage weight of these fractions. The curves resulting from plotting the data given in Table 1 are shown in figure 2. In other distillations

the original and corrected data will not be given, but only the curves obtained by plotting the corrected data; the curves are sufficient to give the complete interpretation of the results, and there are so many distillations recorded that it would be prohibitive to use the space required by the tabulated data.

INTERPRETATION OF DISTILLATION CURVES.

To interpret these curves properly it is necessary to understand the behavior of a mixture of liquids on distillation, and a brief discussion of fractionation by distillation and of distillation curves will therefore be given, to be followed by a discussion of the curves obtained by the distillation of two different turpentines.

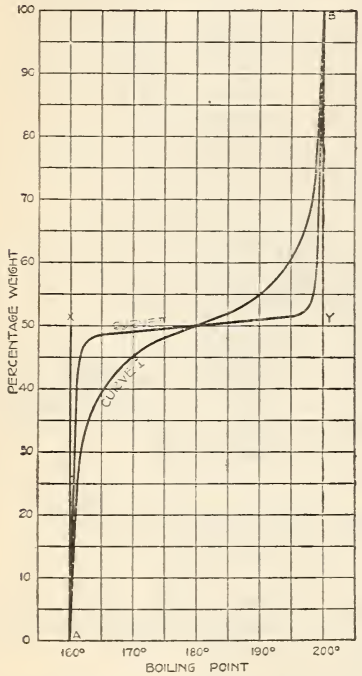

FIG. 3.—Curves illustrating theory of fractional distillation.

THEORETICAL BOILING-POINT CURVES.

Let us assume a mixture of equal quantities of two volatile liquids, A and B, with boiling points 160° C. and 200° C., respectively. If on distilling this mixture a complete separation of the two components was obtained, then the distillation curves formed by plotting the percentage of distillate against the boiling point would be represented by the vertical lines AX and BY (fig. 3): that is, all of substance A in pure condition would distill over first and then the pure substance B.

FRACTIONATION BY ORDINARY DISTILLATION.

Such a complete separation is, however, never obtained, because the boiling point of one liquid is always affected by the presence of another volatile liquid. In this case some of the higher boiling substance B would distill over with A long before the temperature of the distillation reaches 200°, the boiling point of B, and some of the lower boiling substance A would be left in the flask even after the temperature had risen above 160° C. When such a mixture is distilled from an ordinary distilling flask, the distillation curve would therefore be more like curve I in figure 3. This curve shows that the composition of the distillate gradually changes throughout the distillation from pure A to pure B, the first

25 per cent of the distillate being nearly pure A and the last 25 per cent being nearly pure B.

FRACTIONATION BY DEPHLEGMATION.

In order to obtain better separations of A from B in a single distillation some kind of a still head or dephlegmator is used (such as the Hempel column shown in fig. 1) in which the ascending vapors are partially condensed and flow downward in liquid form to the distilling flask. The descending liquid comes in contact with more ascending vapors, and there is an interchange of constituents, some of the low boiling material in the liquid being vaporized and some of the high boiling material in the vapors being condensed, with the result that the vapors which finally leave the top of the dephlegmator contain a larger proportion of the lower boiling material than the vapors which enter the dephlegmator from the flask. In other words, when the dephlegmator is used there is a more complete separation of the component materials. Under such conditions the distillation curve would be more like curve II in figure 3, which indicates about 45 per cent practically pure A, about 10 per cent of a rapidly changing mixture, and the rest practically pure B.

SUMMARY.

This consideration of the boiling-point curve of a mixture of two components may be summed up as follows:

(1) The more complete the separation the more accurately do the curves represent the composition of the mixture.

(2) The more vertical curves indicate a more uniform substance in the distillate.

(3) Curves more nearly horizontal indicate a distillate rapidly changing in composition.

DISTILLATION CURVES OF A GUM TURPENTINE.

There is an analogy between the distillation curves for a turpentine and the theoretical curve in figure 3, but complications arise in the interpretation because the mixture distilled is complex and the separation of some of the constituents is incomplete. Specific gravity and index of refraction are plotted, like the boiling point, against percentage weight, and the three curves are considered together in interpreting the results of the distillation.

The curves in figure 2, which give the results of the distillation of a gum turpentine, might be interpreted, in the light of the previous discussion, as indicating a composition of about 95 per cent of some substance *a*, with boiling point 158° C., specific gravity 0.865,

and index of refraction 1.4714 and about 5 per cent of some other material, *b*, with values of all properties considerably higher (say, specific gravity 0.95, index 1.489). The gradual increase in the values of all the physical properties from the first fraction up to 95 per cent might be thought to be due to a gradually increasing proportion of this high-boiling and heavy material in the distillate (as was the case in the boiling-point curves of fig. 3); but this interpretation is shown to be incorrect by a procedure to be described—a procedure which was carried through for an entirely different purpose (see p. 25).

Figure 13 gives the result of a distillation of a part of the turpentine used in figure 2, which had been redistilled several times in order to remove the high-boiling and heavy material originally present. The curves show that this heavy material, *b*, has been entirely removed, and yet the values for all the physical properties increased to some extent as the distillation progressed, which indicated that the distillate was not a pure substance. Evidently, then, the gradual increase of these values in figure 2 was not due to the presence of *b* in the first 95 per cent of the distillate, but instead there must have been present another substance, *c*, with physical properties only slightly higher than those of *a*, the boiling points of *a* and *c* being so close together that the substances are very incompletely separated by distillation.

This interpretation agrees with the results of recent investigations of the chemical constituents usually present in turpentine. According to Semmler,[1] there may be present in American turpentine besides pinene [2] two other terpenes, camphene and nopinene [3]. The physical properties of these two terpenes have not been accurately determined, but it is sufficient to know that they are all higher than those of pinene. The first 95 per cent of the distillate from this turpentine was probably composed of a mixture of pinene with either camphene or nopinene, or both, and the last 5 per cent was made up of materials with much higher physical properties, probably oxidation products of the terpenes.

In the distillation of turpentine by this method the separation between the terpenes and the high-boiling nonterpenes is sufficiently complete, so that the physical properties of the first fractions are not appreciably influenced by the presence of materials with boiling points of from 30° to 35° higher. The mixture of the terpenes—pinene, camphene, and nopinene—is, however, not sufficiently well separated to make it possible to estimate the proportions of the dif-

[1] "Die Aetherische Oele," Vol. II, pp. 55 and 274.

[2] Boiling point, 155°–156° C.; specific gravity, 0.863; index of refraction, 1.4678.

[3] The physical properties of both about the same at the following values: Boiling point, 160° to 165°; specific gravity, 0.874; index of refraction, 1.4724.

ferent constituents, and in this paper the three together will be designated as "pinene," unless for a special reason it is necessary to mention the other constituents.

DISTILLATION CURVES OF A WOOD TURPENTINE.

The curves obtained by the distillation of a wood turpentine (fig. 54) show it to be so different in composition from the gum turpentine just discussed that new points in the interpretation of the curves are introduced. The first 70 to 75 per cent of the distillate could well be, from the physical properties, a mixture of the same terpenes which are the main constituents of the turpentine shown in figure 2, the slightly lower physical properties being accounted for by smaller proportions of either nopinene or camphene, or both. But between the points where 70 and 95 per cent distill, the specific gravity of the distillate decreases, while the boiling point and index of refraction increase. This indicates the presence of some substance with higher boiling point and higher index of refraction, but with lower gravity than pinene. There is a terpene, dipentene, whose physical properties correspond well with those required by this substance; it has a higher boiling point (175° C.), a lower specific gravity (0.849 at 15° C.), and higher index of refraction (1.471 at 15° C.) than pinene; it is known to be one of the products of the action of high temperatures on pinene;[1] it has been identified as one of the constituents of wood turpentines produced in Finland and Russia;[2] and its presence in American "pine tar oil" has been indicated.[3] It is quite probable, therefore, that the substance whose presence is indicated by the marked decrease in specific gravity of the fractions as the boiling point approaches 175° C. is dipentene and that it is formed from pinene by the high temperature employed in removing the turpentine from the wood.

CHEMICAL IDENTIFICATION OF DIPENTENE.

In order to make sure that dipentene was present in this turpentine, however, an identification by chemical means was carried out. By repeated fractional distillation and final distillation over sodium a considerable quantity of material was obtained with boiling points 172° to 174.1° C., specific gravity 0.8527 at 15° C., and index of refraction 1.4771 at 15° C. Part of this material was treated with bromine in glacial acetic acid[4] and crystals were obtained which, after six crystallizations from ethyl acetate, melted at 125° to 125.5° C. (dipentene tetrabromide 125° to 126° C.), thus substantiating the con-

[1] Wallach, Ann. Chem. 227, 282.
[2] Aschan and Hjelt. Chem. Ztg. 18, 1566.
[3] Kremers, Pharm. Rev. 22, 150.
[4] Heusler-Pond, "Chemistry of the Terpenes," pp. 73 and 95.

clusions regarding the presence of dipentene, which were originally drawn from the physical properties. It seems very likely, therefore, that when a turpentine obtained from the long-leaf pine is distilled by the method described above, a decrease in specific gravity as the boiling temperature approaches 175° C. is a good indication of the presence of dipentene.

COMPLETENESS OF SEPARATION OF CONSTITUENTS.

The exact percentage of dipentene can not be determined from the curves in figure 54, since the separation between the pinene and the dipentene is not sufficiently sharp. There are small quantities of dipentene in the portion distilling between 70 per cent and 80 per cent as shown by the slight decrease in specific gravity, but it is only in the portion coming over after 80 per cent has been distilled that there are comparatively large quantities of dipentene present (as shown by the decided changes in direction in the boiling point and index of refraction curves). The separation between the dipentene and the "heavy oils" is, however, quite complete, and the percentage of the latter can be determined with considerable accuracy. This turpentine contains, then, 95 per cent of terpenes (containing approximately 80 per cent pinene and 15 per cent dipentene) and 5 per cent of heavy, high boiling oils, probably nonterpenes.

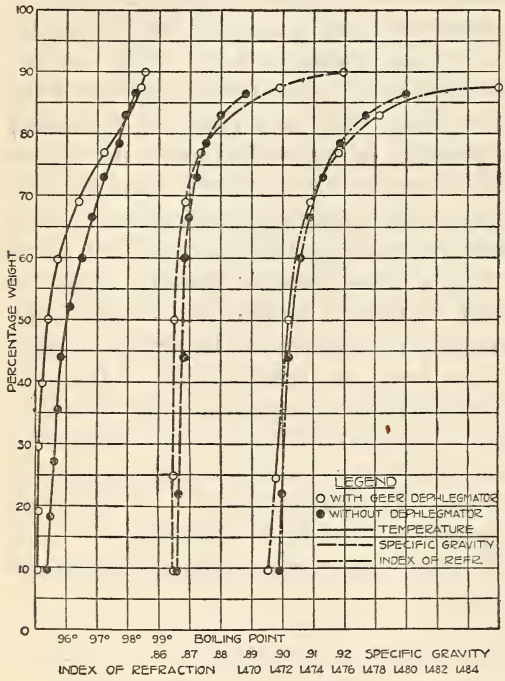

FIG. 4.—Comparison of fractionation obtained in steam distillation with a Geer dephlegmator and without a dephlegmator.

COMPARISON OF FRACTIONATIONS BY DIFFERENT METHODS.

In order to show the advantages gained by the use of a dephlegmator, and by the use of direct distillation instead of steam distillation, the following distillations were carried out on the same turpentine: (1) Steam distillation without a dephlegmator; (2) direct distillation without a dephlegmator; (3) steam distillation with a

Geer dephlegmator as described in Forest Service Circular No. 152; and (4) direct distillation through a five-bulb LeBel-Henninger dephlegmator. The last-named dephlegmator will not be described, because another form was afterwards adopted as most suitable for general work.

STEAM DISTILLATION WITH AND WITHOUT A DEPHLEGMATOR.

In figure 4 are plotted together on one sheet for better comparison the curves obtained by steam distillation, both with and without a dephlegmator. The curves showing the results obtained by the use of a dephlegmator indicate the better fractionation, since they are more nearly vertical and have lower values over the first part of the distillation, and the breaks in the general direction are more marked than in the curves which give the results obtained by steam distillation without a dephlegmator.

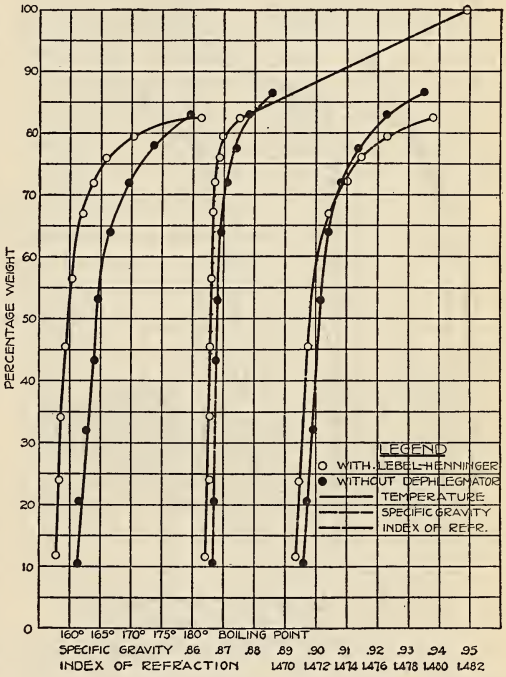

FIG. 5.—Comparison of fractionation obtained in direct distillation with a Le Bel-Hinninger column and without a dephlegmator.

DIRECT DISTILLATION WITH AND WITHOUT A DEPHLEGMATOR.

A still greater effect obtained by the use of a dephlegmator is indicated in figure 5, where are plotted together the curves from two direct distillations, one with and one without a dephlegmator. Here the differences in the position and direction of the curves and therefore in the fractionation are even more marked than in figure 4.

STEAM AND DIRECT DISTILLATION WITH DEPHLEGMATORS.

Figure 6 gives a comparison of the fractionation obtained by steam distillation through a Geer dephlegmator with that by direct distillation through a Le Bel-Henninger dephlegmator. In the direct-dis-

tillation curves there are all the evidences of better fractionation, i. e., lower values for the physical constants of the fractions over the first part of the distillation, more nearly vertical curves, and sharper breaks in the direction of the curves. On account of the better fractionation it is possible to judge the composition of the turpentine with a considerable degree of accuracy and it apparently contains very nearly 80 per cent of pinene, the remainder being heavy oils with all the physical properties much higher. From the steam-distillation curves, on the other hand, it would be impossible to make an accurate judgment of the proportion of pinene present in the turpentine, because the separations are so incomplete and the curves change direction so gradually. This distillate is practically pure pinene up to about 70 per cent, but for some distance beyond that point it is an indefinite mixture of pinene with heavier and higher boiling materials.

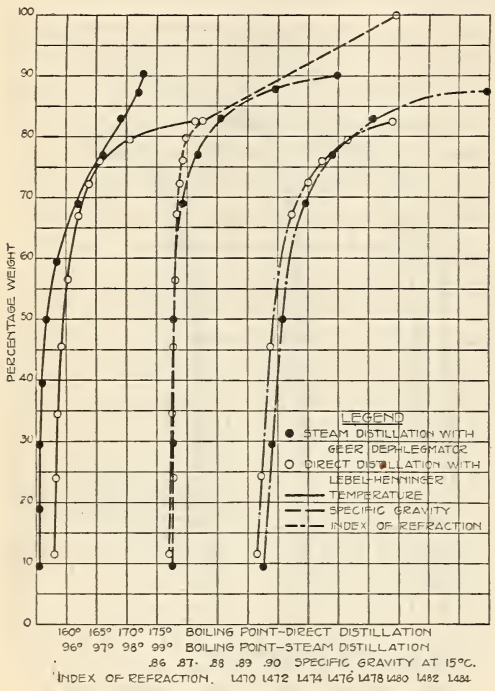

FIG. 6.—Comparison of fractionation obtained by steam distillation with a Geer dephlegmator and direct distillation with a Le Bel-Henninger dephlegmator.

Similar distillations were made on another kind of turpentine (refined turpentine No. 5) giving even more striking differences in the separations obtained. Figure 7 shows the results obtained by fractionation of three samples of the same turpentine (1) by steam distillation with a Geer dephlegmator, (2) by direct distillation without a dephlegmator, and (3) by direct distillation with a Le Bel-Henninger dephlegmator, the three sets of curves being plotted together on one sheet for easier comparison. The curves obtained by steam distillation with a dephlegmator, and by direct distillation without a dephlegmator show very simlar characteristics; there are no rapid changes in direction until about 90 per cent is reached and then there is a rapid increase in all the physical constants; that is, these curves indicate about 90 per cent pinene and about 10 per cent of material with all physical constants higher. The curves obtained by direct distillation with a dephlegmator are, however, quite

different; they indicate that there are three main constituents of this turpentine sufficiently different in boiling points and other properties so that approximate determinations can be made of the proportion of each, these proportions being about 80 per cent of pinene, 15 per cent of dipentene, and 5 per cent of heavy residue. In the distillation by the first two methods the dipentene was not sufficiently well separated from the other constituents so that its presence was sharply indicated, the very slight and very gradual decrease in the specific gravity over the first 80 per cent of the distillation being the only sign of the presence of such a substance.

Another comparison of the results obtained by steam and direct distillation, both through a dephlegmator, is given in figure 8, in this case on a still more complex turpentine. The curves obtained by the direct distillation with a Le Bel-Henninger dephlegmator indicate that this turpentine is composed of about 11 per cent "light oils" (with boiling points below those of pinene), about 32 per cent of pinene, about 22 per cent of dipentene, and 35 per cent of heavy oils. The separation between the pinene and the dipentene was not very sharply indicated—that is, the breaks in the direction of the curves are not very marked—but the amount of light oils, of turpentine oils (pinene and dipentene), and of heavy oils are quite accurately determined. In the steam-distillation curves, however, no sharp separation of the turpentine into its constituents are shown; that is, there are no sharp breaks in the curves. The presence of dipentene is not even indicated qualitatively, and the proportion of heavy oils (as in fig. 6) can not be judged within 8 to 12 per cent.

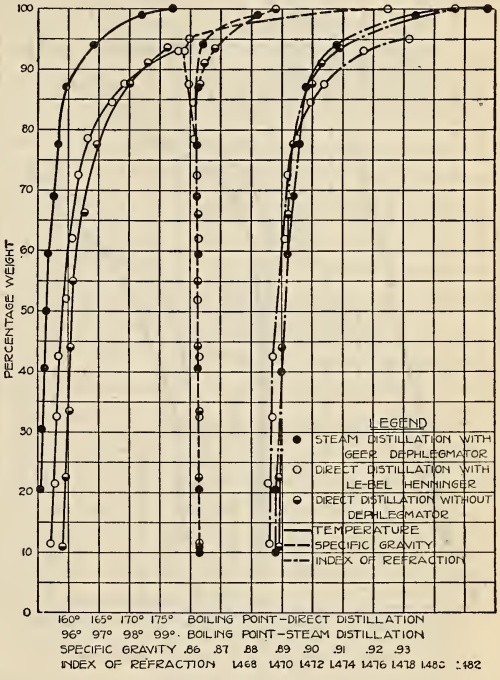

FIG. 7.—Comparison of fractionation obtained by (1) steam distillation with a Geer dephlegmator, (2) direct distillation with a Le Bel-Henninger dephlegmator, and (3) direct distillation without a dephlegmator.

These examples of the results obtained in the fractionation of three different turpentines by different methods of distillation have shown

very clearly that, so far as the completeness of the separations and the corresponding ease and accuracy of the interpretation of the results are concerned, direct distillation through a dephlegmator is the best distillation method for the analysis of turpentine.

CHANGES IN COMPOSITION DURING DISTILLATION.

A possible objection to direct distillation with dephlegmators[1] is that the higher temperatures required are likely to decompose some of the oil during the distillation so that the fractions will not represent the true composition of the original material. In those distillations in which the same turpentine was distilled direct and by steam there were no evidences of decomposition in any case except that the residues left in the distilling flask were usually darker in color when direct distillation had been used; the differences in the curves obtained by the two methods were of such a nature as would indicate only a different fractionation.

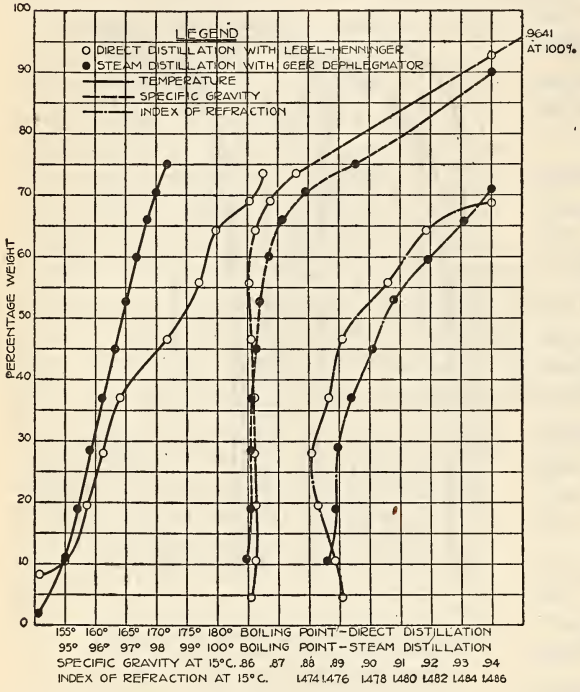
LEGEND
O DIRECT DISTILLATION WITH LEBEL-HENNINGER
● STEAM DISTILLATION WITH GEER DEPHLEGMATOR
TEMPERATURE
SPECIFIC GRAVITY
INDEX OF REFRACTION
.9641 AT 100°
PERCENTAGE WEIGHT
155° 160° 165° 170° 175° 180° BOILING POINT—DIRECT DISTILLATION
95° 96° 97° 98 99° 100° BOILING POINT—STEAM DISTILLATION
SPECIFIC GRAVITY AT 15°C. .86 .87 .88 .89 .90 .91 .92 .93 .94
INDEX OF REFRACTION AT 15°C. 1.474 1.476 1.478 1.480 1.482 1.484 1.486

FIG. 8.—Comparison of fractionation obtained by direct distillation with a Le Bel-Henninger dephlegmator and steam distillation with a Geer dephlegmator.

CHANGES IN PHYSICAL PROPERTIES AT CONSTANT TEMPERATURES.

CRUDE WOOD TURPENTINE.

In order to obtain some idea of the comparative effects of different methods of distillation on the physical properties of turpentines, two samples of the same turpentine (turpentine No. 4) were boiled under conditions similar to those of steam and direct distillation—that is,

[1] This objection is mentioned in Forest Service Circular 152, "The Analysis of Turpentine by Fractional Distillation with Steam," by William C. Geer.

with and without water—and the specific gravity and index of refraction were determined at regular intervals; in both cases a well-cooled reflux condenser was used so that the loss was negligible. The effects of boiling under these two sets of conditions are shown graphically in figure 9. By boiling with water at a temperature of about 94° C., the specific gravity of the turpentine was increased very slightly the first hour and after that decreased very slightly every hour until the boiling was stopped. By the boiling without the presence of water at a temperature of about 162° C., the gravity increased at the rate

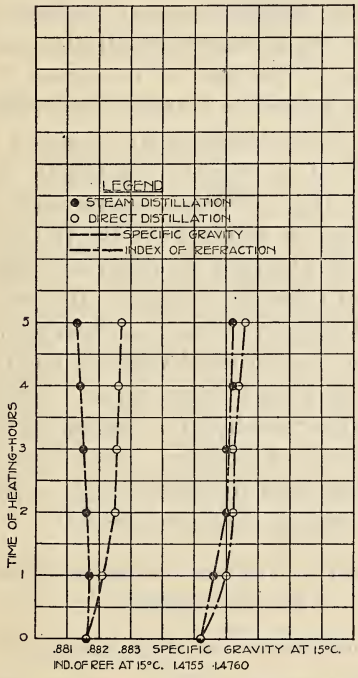

FIG. 9.—Effect of boiling with water (steam distillation) and of boiling without water (direct distillation) on the specific gravity and index of refraction of crude wood turpentine.

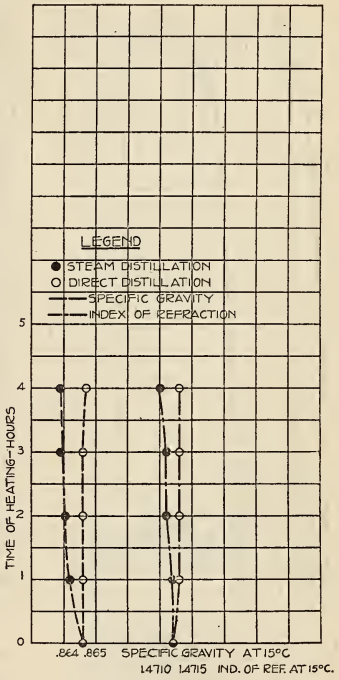

FIG. 10.—Effect of boiling with water (steam distillation) and of boiling without water (direct distillation on the specific gravity and index of refraction of refined wood turpentine.

of 0.00045 per hour for the first two hours, and then at a much slower rate. The index of refraction was increased considerably by both methods of boiling during the first two hours and then more slowly.

REFINED WOOD TURPENTINE.

The results from a similar series of experiments on another turpentine (turpentine No. 5, the analysis of which is shown in fig. 7) are expressed graphically in figure 10. Here the changes in the physical properties due to methods of boiling are less than were shown in

figure 9, being within the limit of possible experimental errors. But the same general tendency of the specific gravity to be slightly increased by the direct boiling and slightly decreased by the boiling with water is shown, as in figure 9. The index of refraction is, however, slightly decreased by the boiling with water instead of being increased.

The effect of the boiling on the physical properties of the turpentines is apparently not very great in either case, but for two reasons the results obtained are not conclusive: (1) The temperatures to which the turpentines were subjected were only as high as would prevail at the very beginning of distillation, and therefore, in the case of the direct distillation, probably do not come within 40° C. of the temperatures reached at the end of a regular fractional distillation; (2) different components of the turpentine might have the physical properties changed in different directions and thus the changes in the properties of the turpentine as a whole would not show the actual changes in composition which had taken place. Therefore, another method for comparing the changes in composition due to steam distillation and direct distillation was carried out as described below.

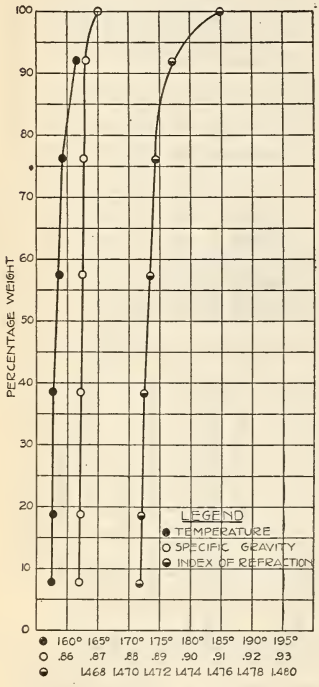

FIG. 11.—Alteration in physical properties of a crude wood turpentine due to direct distillation.

CHANGES IN PHYSICAL PROPERTIES UNDER FRACTIONATION.

DIRECT DISTILLATION OF CRUDE TURPENTINE.

Crude turpentine No. 4 was repeatedly redistilled by direct distillation through a Le Bel-Henninger dephlegmator. Each time the heavy residue left in the flask and as much of the distillate as showed especially high physical properties were rejected. The first distillation was similar to the direct distillation shown in figure 6, and the fractions up to 79.5 per cent formed the material for the next distillation, the residue and the last fraction of the distillate being rejected. The curves showing the course of the third and fourth distillations were practically identical and are both represented by the curves in figure 11. All the heavy oils present in the original turpentine must have been removed by the first two distillations.

otherwise the physical properties of the residue would have been higher in the third distillation than in the fourth. Since the original heavy oils had been completely removed, the higher physical properties of the residue in the third and fourth distillations must be due to the heavy oils formed during the course of the distillations. The difference in the values of the physical constants between the last fraction and the residue in figure 11 is therefore an approximate measure of the change in composition due to the temperature of the distillation. The lack of any marked difference in properties between the first and second fractions indicates that there was no appreciable decomposition into substances with lower boiling points.

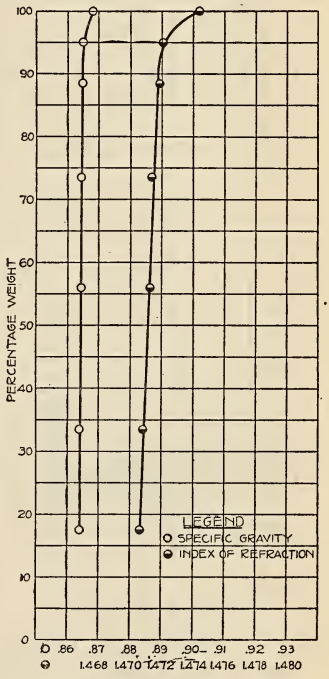

FIG. 12.—Alteration in physical properties of a crude wood turpentine due to steam distillation.

STEAM DISTILLATION OF CRUDE TURPENTINE.

In order to obtain, for comparison, the change in composition due to distillation with steam, all the material represented by figure 2, except the residue, was twice distilled by steam through a Geer dephlegmator. The curves for these two distillations were practically identical and are shown in figure 12. Reasoning in the same way as above the difference in physical properties between the last fraction and the residue indicates the change in composition due to distillation. This change is appreciable in the case of the steam distillation, but is somewhat less than in the direct distillation.

DIRECT DISTILLATION OF GUM TURPENTINE.

The same distillation was made on a gum turpentine (the one whose analysis is shown in figure 2). In this, as in case of the wood turpentine, the third and fourth distillations gave nearly identical curves, which are shown in figure 13. The amount of change in composition is also very nearly the same as in the case of the wood turpentine shown in figure 11.

It is evident, then, that, under the conditions prevailing in the distillation shown in figures 11 to 13, the amount of change in composition during analysis is very slight, either in steam or direct distillation. This change apparently consists in the polymerization of a portion of the terpenes to substances with higher physical constants,

and seems to take place mostly during the very last part of the distillation when the amount of oil in the distilling flask has become very small and when there is, therefore, a better chance for the sides of the flask to become superheated.

CHANGES IN COMPOSITION AND INTERPRETATIONS OF CURVES.

TURPENTINES CONTAINING NO HEAVY OILS.

When a turpentine containing no heavy oils is distilled by direct heat the undistilled residue left in the flask will contain a small amount of heavy oils, owing to changes occurring during the distillation, and the specific gravity and index of refraction of this residue will be higher than those of the last distilled fraction; the curves will, therefore, seemingly indicate that small amounts of heavy oils were present in the original turpentine, but from the curves of figures 11 to 13 the effect of the changes, which occurred during the distillation, can be determined, and the interpretation of the curves can be altered to correspond. For instance, in the distillation of 95 per cent of a turpentine containing no heavy oils, the production of heavy oils during the distillation will be sufficient to increase the gravity and index of the residue of 5 per cent by 0.0035 and 0.0040, respectively. Of course, if the residue is made smaller—say 2 per cent—then the apparent effect would be greater, since there is a chance for more polymerization during the distillation of that portion between 95 and 97 per cent; and the proportion of heavy oil to turpentine oil in the undistilled residue is increased—and hence the physical properties increased—as the distillation progresses. It is therefore necessary to leave about 5 per cent of oil undistilled in order to be able to correct accurately for the effect of polymerization.

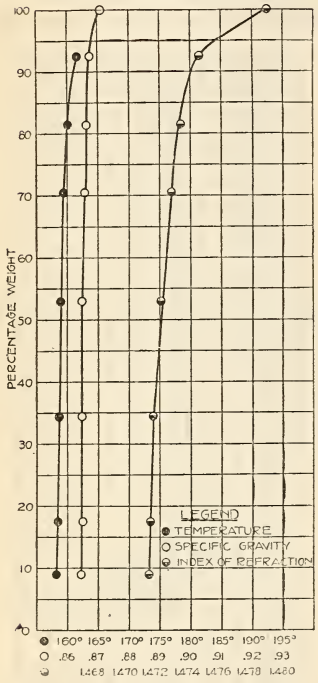

FIG. 13.—Alteration in physical properties of a gum turpentine due to direct distillation.

TURPENTINES CONTAINING HEAVY OILS.

When, however, the turpentine to be distilled contains some heavy residue (as for instance in fig. 2) the conditions are different; the terpenes may all be distilled over, and the residue left in the flask

would then be all heavy oils. These heavy oils might be changed by the heat, either more or less than the terpenes were in figures 11 to 13, but there is really no necessity for determining this change accurately because a small change in the physical properties does not effect the interpretation of the curves. For instance, if in figure 2 the gravity of the residue had been 0.930 instead of 0.945, the composition of the turpentine as interpreted from the curves would still have been 95 per cent pinene and 5 per cent heavy residue; that is, a gravity of 0.93 is so much higher than that of the terpenes that the presence of a considerable amount of terpenes in the residue is excluded; and the only possible interpretation of the composition of the residue is that it does not contain terpenes in considerable quantities.

The change in composition of a turpentine during analysis by direct distillation is, therefore, without effect on the interpretation of the results, except in case there is no high boiling and heavy residue present in the original material; and in this case the approximate effect is known and the results can be corrected.

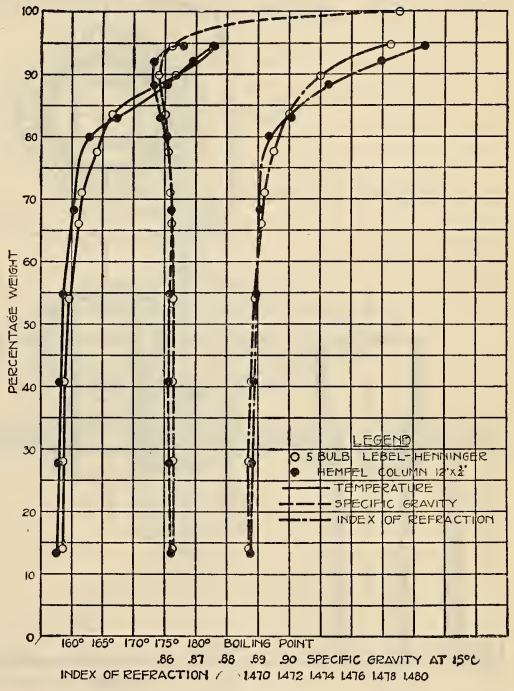

FIG. 14.—Comparison of fractionation with Le Bel-Henninger and Hempel column dephlegmators.

CHOICE OF A DEPHLEGMATOR.

The Le Bel-Henninger dephlegmator has been used with good results in many turpentine analyses; it is efficient in fractionating power, and when properly constructed gives no trouble by filling up with liquid; the only objections to it are that it is expensive and fragile. The simplest, least expensive, and least fragile dephlegmator is of the Hempel column type, and several different sizes of Hempel columns were tried to find if a practicable sized Hempel would give as good separations as the Le Bel-Henninger. It was found that the Hempel column, shown in figure 1, gave slightly better separations than the five-bulb Le Bel-Henninger and a com-

parison between the results obtained by the use of these two dephlegmators is shown in figure 14. The main difference between the curves obtained by the two types of dephlegmators is in the specific gravity in the vicinity of 90 per cent; the fractions obtained by distillation through the Hempel column have a lower gravity over this part of the curve, indicating a purer dipentene and therefore better fractionation; the sharper break in the curves at about 80 per cent also indicates better fractionation. On account of the simplicity and cheapness of the Hempel column as well as its better fractionation, it is recommended as the preferable dephlegmator for turpentine

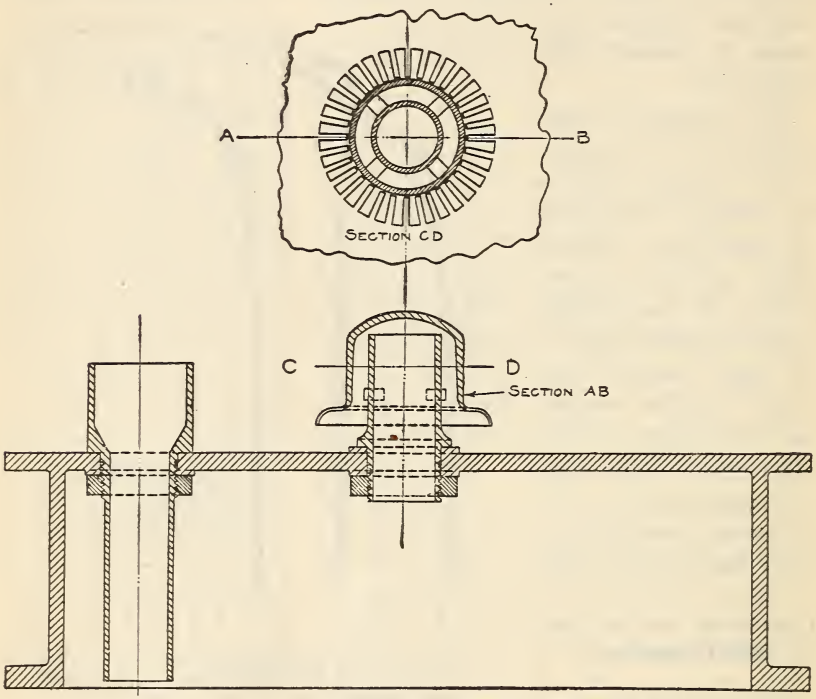

FIG. 15.—Boiling cap section.

distillations. This type of dephlegmator has been used in making many of the distillations recorded in the following pages, and has given very satisfactory results.

REFINING.

Five samples of crude wood turpentine were refined; these were collected from commercial plants using widely varying processes, a brief description of which will be given. The apparatus used in the refining and the method of conducting the distillations were similar for all the samples.

DESCRIPTION OF APPARATUS.

The refining still was of the continuous type with two phases, giving two distilled products and one undistilled residue. It was designed by the makers especially for this work, since stills of this type for the refining of turpentine had not previously been used or manufactured in this country.

BOILING-CAP SECTIONS.

The boiling-cap section, shown diagrammatically in figure 15, is the typical and important division of the column, the other kinds of sections being modifications of this typical section. Each section

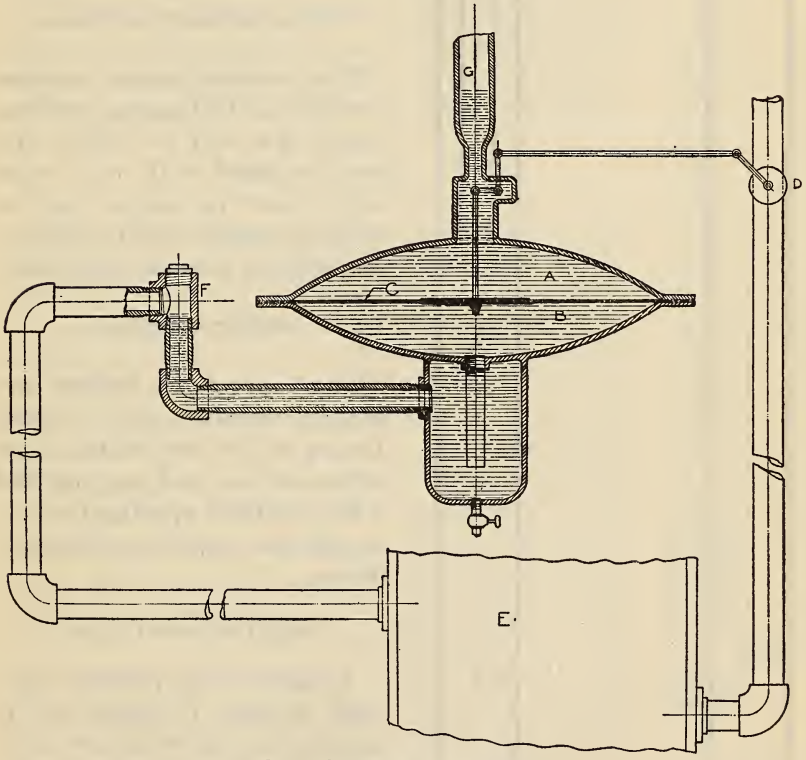

FIG. 16.—Pressure regulator.

is 14 by 12 inches inside diameter, and is supplied with eight boiling caps and two return pipes. The liquid level on each section is kept even with the top of the return pipes, and the vapors from the section below are made to pass through this liquid by means of the boiling caps; the rim of each cap is slotted so that the vapor passes through the liquid in small bubbles, and good contact between the ascending vapor and the descending liquid is thus obtained.

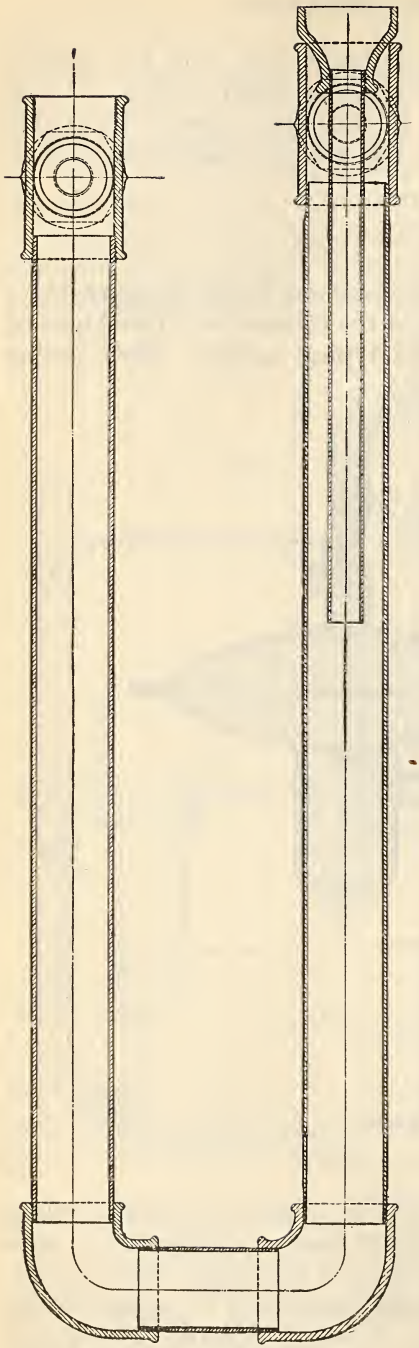

FIG. 17.—Separator.

REFLUX-CONDENSER SECTIONS.

The reflux-condenser sections are really a combination of a boiling-cap section with a reflux condenser; that is, they are similar to figure 15, except that below the return pipes there is a chamber filled with copper tubes, around which the vapors must pass and through which water is kept flowing.

STEAM-CHAMBER SECTIONS.

The steam-chamber sections are like the boiling-cap sections, except that they are higher and are furnished with two steam inlets near the bottom and an opening near the top for connection with the pressure regulators.

OUTLET SECTIONS.

The vapor-outlet sections are simply chambers for covering the top of the last boiling cap or reflux section, and are provided with a suitable opening for conveying the vapors to the condenser.

PRESSURE REGULATORS.

A sketch of the pressure regulator is given in figure 16. It consists essentially of two chambers, A and B, separated by a rubber diaphragm. Any motion of the diaphragm such as might be caused by a change of pressure in either chamber is communicated by the system of levers to the steam valve D. For in-

stance, if there is an increase of pressure in the steam chamber E, there is a corresponding increase of pressure on the bottom of the diaphragm and the diaphragm moves upward, closing the valve D until the pressure is again normal in E.

SEPARATORS.

The separator, figure 17, is the same in principle as the ordinary automatic oil and water separator used in practice, but it is made much more compact in order that only a small amount of oil can be retained in it at one time. This apparatus can be made entirely from ordinary iron pipe and pipe fittings. A separator like that shown in the drawing, with a total length of 3 feet, and with the main tube made of 2½-inch iron pipe, was sufficient for the separation of 20 to 23 gallons of refined turpentine from about the same amount of water per hour.

SPEED INDICATORS.

The speed indicator,[1] figure 18, is based on the principle that there is a definite relation between the rate of flow of a liquid through a small aperture and the pressure of the liquid at the aperture. The liquid, as for instance the refined turpentine, enters the indicator from the separator through A. The only outlet for the liquid is the tube C, which may be entered from the top or through the aperture D, this aperture is made small enough so that, with the normal flow of the liquid, it is necessary for the liquid level to rise some distance in the tube B in order that the pressure may be sufficient to make the liquid flow through D at the same rate it enters through A. The height of the liquid level in B is a measure of the rate of flow through D, and the relationship between these factors is obtained by calibration; that is, by measuring the rate of flow from C while the liquid level is maintained at constant measured distances above D. The calibration curve for the crude-turpentine indicator is shown in figure 19.

FIG. 18.—Speed indicator.

[1] This apparatus can be made almost entirely from ordinary iron pipe and pipe fittings. The pipe C should, however, be of brass so that the aperture D may not be changed in size by rusting and, of course, the tube B must be of glass. The method of fastening the glass tube into the iron parts is shown in the drawing; E is a support of tin plate or other thin, easily shaped, metal soldered to the nipple in order to support the tube B and packing F; G is a thin layer of litharge and glycerin cement, which makes the joint oil or water-tight.

The other parts of the apparatus were of standard design and require no special explanation.

GENERAL ARRANGEMENT AND OPERATION OF APPARATUS.

A diagram of the general arrangement of the apparatus is given in figure 20. The fractionating column A is divided into the two separate columns A_1 and A_2 at the place marked by the heavy line. A_1 and A_2 are made up of the different kinds of sections already described, as follows: A_1 from the bottom upward, 1 steam chamber

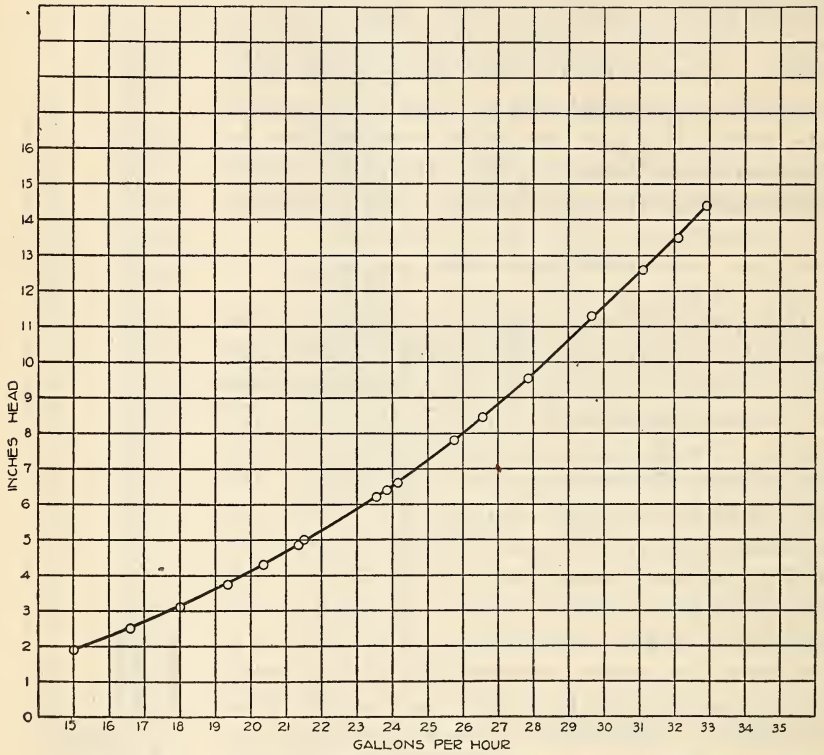

FIG. 19.—Calibration curve for crude turpentine speed indicator.

section, 5 boiling-cap sections, 2 reflux-condenser sections, and 1 outlet section. A_2 is similarly made up of 1 steam chamber section, 13 boiling-cap sections, 3 reflux-condenser sections, and 1 outlet section.

The tank for crude oil F is connected through the pump G with the reservoir D; the overflow pipe from D, through valve 9, furnishes an air outlet for D while it is being filled and serves the purpose also of notifying when D is full; the return pipe through valve 10 also makes it possible to draw out any material from D directly into the tank F. The reservoir D is simply a 110-gallon steel drum, arranged on the principle of a Mariotte's bottle in order to keep the flow of

crude turpentine through valve 1 constant, whatever the level of crude turpentine in D. The reservoir D having been filled and valve 10 closed, valve 1 is opened until the crude turpentine is running at the required speed as registered on the speed indicator J, say 25 gallons per hour. The crude turpentine then flows through the feed heater C, where it is heated by steam from valve 2 to a temperature of about 95° C., and enters the upper column A_1 at the fourth boiling cap section as indicated. The steam supply is now adjusted by the pressure regulator H_1, and the water in the reflux sections by valve 4, so that the distillate leaving the top of column A_1 is running at the required speed as indicated on the speed indicator J_2. The speed required is determined from the analysis of the crude turpentines;

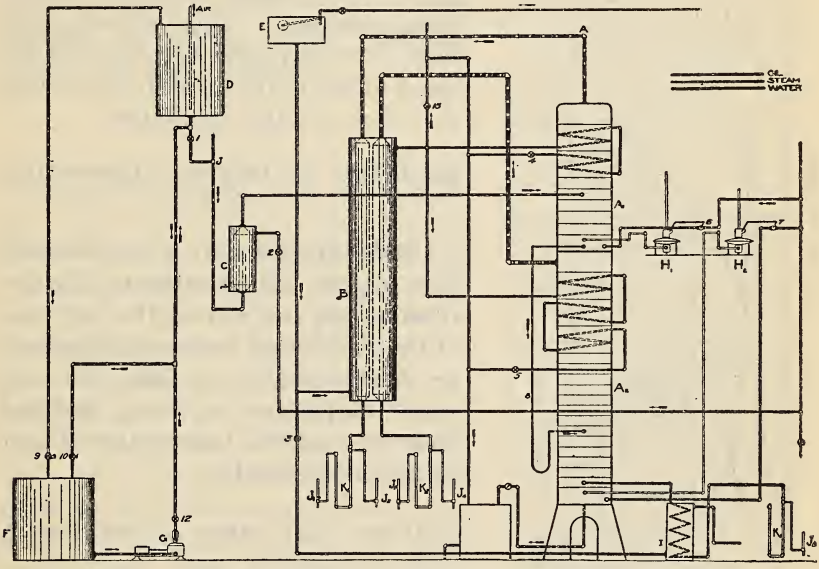

FIG. 20.—General arrangement of apparatus for refining crude turpentine.

for instance, if 5 per cent of low-boiling material which it is desired to remove from the refined turpentine is present in the crude, then it is only necessary to adjust the speed of the first distillate to 5 per cent of the speed of the crude.

The portion of the crude not distilled in column A_1 flows from the bottom section through the trapped pipe 8 into the column A_2 at the sixth boiling cap section. Here the distillation process is repeated as in the top column, the water and steam supplies being adjusted by valve 5 and the regulator H_2, respectively, so that the distillate leaves the top of A_2 at the required rate.

The undistilled residue or "tails" runs out in liquid form from the first boiling cap section, is cooled in the tails cooler I, separated from

the water, and the speed measured in the indicator J_3. The speed of the tails is not directly controlled, but is dependent upon the speeds of the other products, being equal to the speed of the crude, minus the sum of the speeds of the two distillates.

A constant head for the water supply is maintained by means of the float valve in the reservoir E, so that when the valves 4, 5, and 13 are once adjusted the flow of water through the condenser B and therefore through the refluxes of A_1 and A_2 will be constant. The pressure regulators H_1 and H_2 are used to maintain a constant pressure of steam in the bottom section of the columns A_1 and A_2, respectively, and therefore the speed of the distillates, once properly adjusted, should remain constant. There were in most cases, however, small variations in the speed of the different products during the course of the distillation.

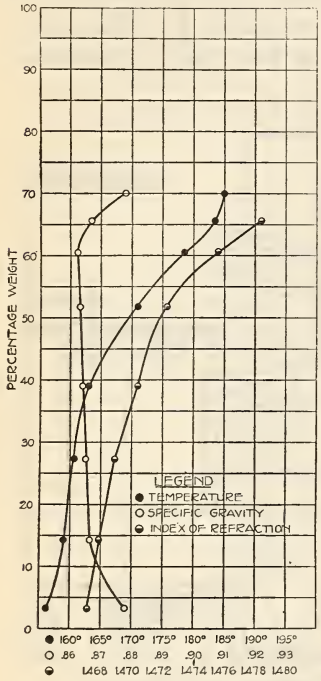

FIG. 21.—Boiling point, specific gravity, and index of refraction curves for crude turpentine No. 1, untreated.

REFINING OF CRUDE TURPENTINE NO. 1.

Crude turpentine No. 1 was obtained from a plant using the destructive distillation process; during the first part of the distillation, however, the retorts are heated slowly, so that while the crude turpentine is being distilled from the wood the temperature is kept as low as is feasible.

ANALYSIS AND CHEMICAL TREATMENT.

The analysis of the crude turpentine is given in figure 21. The odor of the first four fractions was very disagreeable, and the color was a dark yellow; these two things, in connection with the high gravity indicated the impossibility of obtaining by distillation alone any refined turpentine of good quality from this part of the crude, although the boiling points were mostly within the range of a good turpentine. Because it was probable that the contaminating material could be removed by treatment with alkali, the original crude turpentine was agitated with a warm caustic soda solution until action ceased.

The analysis of the treated crude is shown in figure 22. The gravity of the first few fractions was decreased and the index of refraction was increased by the treatment; the color and odor of all the fractions

were also improved. The first fraction of the treated crude, however, had a more disagreeable odor and more color than the other fractions; the second fraction still retained these undesirable qualities, but to a lesser degree; the rest of the fractions were practically colorless and had only slight traces of the strong odor of the first fraction. Since that portion of the distillate which had the undesirable properties also had lower boiling points than the rest of the material, it seemed likely that the undesirable portion could be separated by distillation, with a consequent improvement in the properties of the refined turpentine.

The heavy oils began to come over in quantity at about 70 per cent and the distillate beyond this point was practically free from terpenes.

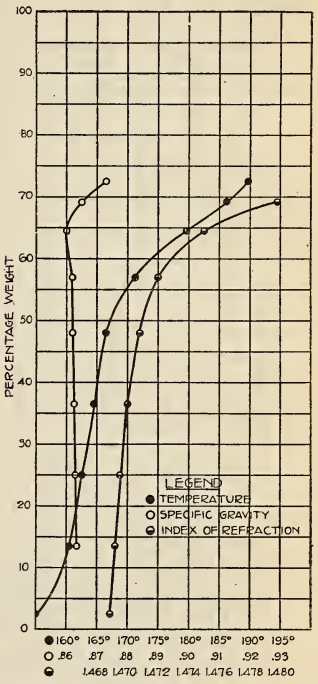

FIG. 22.—Boiling point, specific gravity, and index of refraction curves for crude turpentine No. 2, after treatment with caustic soda solution.

DISTILLATION.

It was decided therefore to separate this crude turpentine by the refining process into two distilled products and a residue, as follows: (1) "Light oils" or "heads" with boiling points below those of turpentine, 5 per cent; (2) refined turpentines or "hearts," 65 per cent; and (3) "heavy oils" or "tails" with boiling points and gravity above those of turpentine, 30 per cent. In order to secure such a separation in the refining still it was necessary to regulate the flow of the different products to the following speeds (the crude turpentine running at 25 gallons per hour):

For heads 5 per cent of 25, or 1.25 gallons per hour.
For hearts 65 per cent of 25, or 16.25 gallons per hour.
For tails 30 per cent of 25, or 7.5 gallons per hour.

In the distillation of this turpentine and all others as well the first runnings of the distillates were caught separately until the adjustment was completed, because the composition of the products would vary greatly at first. The analyses shown hereafter represent the composition of the products obtained after the still was properly adjusted and running smoothly. For instance, this run on turpentine No. 1 occupied about $4\frac{1}{2}$ hours, but the products shown in the analyses were obtained during a little less than 4 hours of this time.

PRODUCTS OF DISTILLATION.

The analyses of the products obtained from the distillation of crude turpentine No. 1 are shown in figures 23, 24, and 25.

HEADS.

The heads (fig. 23) vary greatly in composition, and approximately the first 70 per cent have higher indices of refraction, and

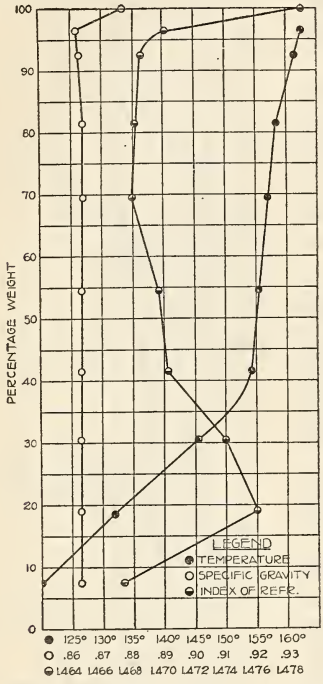

FIG. 23.—Boiling point, specific gravity, and index of refraction curves for "heads" obtained in refining of crude turpentine No. 1.

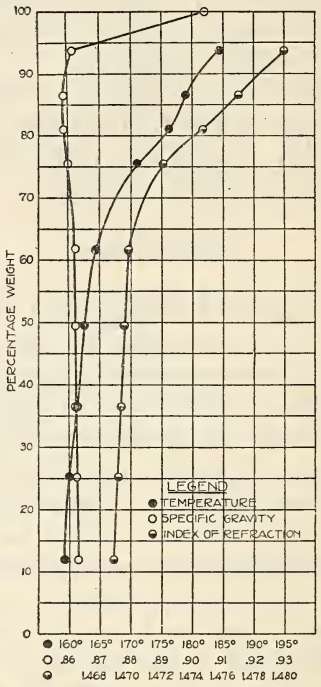

FIG. 24.—Boiling point, specific gravity, and index of refraction curves for "hearts" obtained in refining of crude turpentine No. 1.

lower boiling points, than the first fraction of the hearts; this portion of the distillate also had a darker color and more disagreeable odor than the fractions above 70 per cent. That portion above 70 per cent could well be included in the hearts without affecting the properties of the latter, but probably it is not possible to separate completely so small an amount of heads as were present in the crude, 2.5 to 3.0 per cent, without removing some of the hearts at the same time.[1]

[1] The heads, on account of the method of their production, could not contain any heavy oils, and the higher physical properties of the residue in this analysis (and in the analyses of all the other heads) must be due to polymerization during the distillation (see p. 26).

HEARTS.

The analysis of the hearts is shown in figure 24; there is apparently no material in the hearts with boiling points below 158° C., and the color and odor of the first fractions were not markedly different from those of the next few fractions; that is, the separation of the heads from the hearts was complete. This separation of the low boiling constituents improved both the color and odor of the refined turpentine, making it almost colorless and leaving only a faint trace of the "destructive distillation" odor. There was a small amount, about 6 per cent, of heavy material in the hearts, showing an insomplete separation from the tails.

TAILS.

The tails were analyzed (fig. 25) only to determine how good a separation was obtained between the tails and the hearts. All the properties of the first fraction (9 per cent) of the tails were higher than any fraction of the hearts, except, of course, the residue. But since the composition of the distillate was changing rapidly at this point (the curves all slanting decidedly), it is probable that a small amount of this first fraction was composed of material with properties the same as some portion of the hearts; perhaps 3 to 4 per cent of the tails was composed of materials which should have been in the hearts.

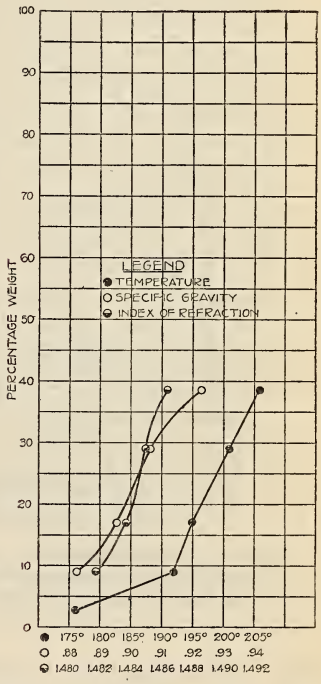

FIG. 25.—Boiling point, specific gravity, and index of refraction curves for "tails" obtained in refining of crude turpentine No. 1.

REFINING OF CRUDE TURPENTINE NO. 2.

Crude turpentine No. 2 was produced at a plant using "lightwood" as a raw material. The process of distillation was the steam process and was different from the usual steam process only in the size of the chips, which were smaller, and in the greater steam pressure used, which was about 50 pounds.

ANALYSIS.

The analysis of this crude is shown in figure 26. There were no evidences in this crude of low boiling material similar to that in

crude turpentine No. 1, but the odor of the first fraction was quite different from the second, and it was decided to separate a small amount of heads in order to find if the odor of the hearts was improved. This crude turpentine is seen to contain about 60 per cent pinene, 8 per cent dipentene, and 32 per cent heavy oils. It was decided to attempt to obtain about 4 per cent of heads, which would leave about 64 per cent of turpentine material to be separated as hearts.

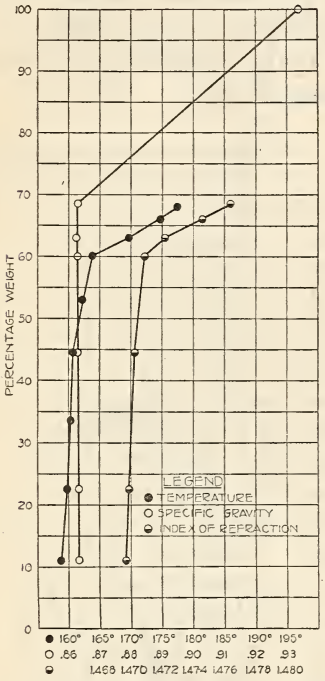

FIG. 26.—Boiling, specific gravity, and index of refraction curves for crude turpentine No. 2.

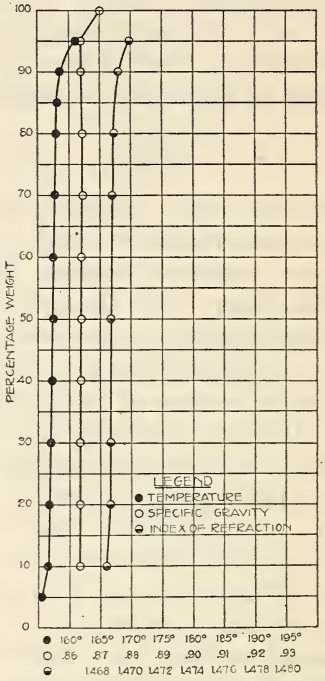

FIG. 27.—Boiling point, specific gravity, and index of refraction curves for "heads" obtained in refining of crude turpentine No. 2.

DISTILLATION.

The crude was run into the still at a speed varying from 24.8 to 25 gallons per hour; the heads were kept as close as possible to 1 gallon per hour (varying from 0.5 to 1.5 gallons per hour), and the hearts varied from 15.7 to 16.1 gallons per hour. Except for the rather large variation in the heads, the distillation seemed to run smoothly.

PRODUCTS.

The analyses of the products are given in figures 27, 28, and 29.

HEADS.

Although the difference in odor between the heads and the hearts was quite noticeable, they did not show any great difference in other properties; the odor of the first 10 per cent of the heads was also somewhat different from the rest of the fractions. The amount of material present in these heads with properties different from the main part of the turpentine (hearts) is therefore very small in pro-

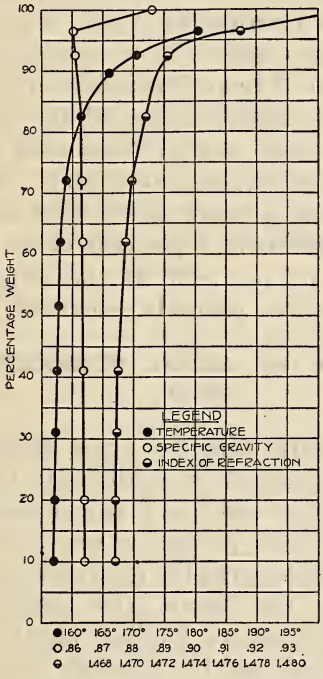

FIG. 28.—Boiling point, specific gravity, and index of refraction curves for "hearts" obtained in refining of crude turpentine No. 2.

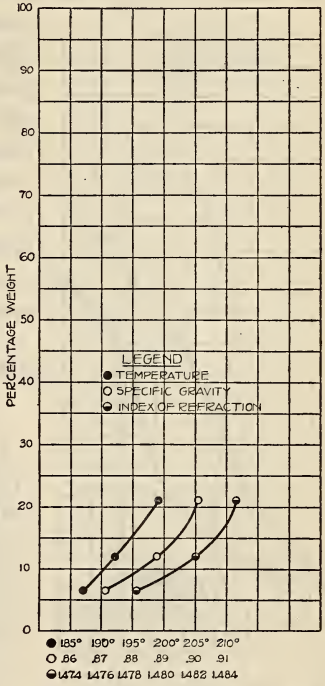

FIG. 29.—Boiling point, specific gravity, and index of refraction curves for "tails" obtained in refining crude turpentine No. 2.

portion to the original crude, so small that it is impracticable and really unnecessary to separate it.

HEARTS.

The hearts contain only about 3.5 per cent of heavy material, and the gravity of this portion is only slightly greater than that of the main part of the hearts, the gravities being 0.885 and 0.863, respectively, which shows a very satisfactory separation of hearts and tails.

TAILS.

The tails, however, contain a small amount of material which might have been included in the hearts. The properties of the first fraction of the tails (7 per cent) are higher than any portion of the hearts except the residue, but the difficulty of completely separating in one distillation a small amount of turpentine material, from a large proportion of higher boiling material like the "pine oil," and the fact that the properties of the distillate were changing rapidly when this fraction was taken both indicate that there was a considerable proportion of turpentine material present in this first fraction of the tails. Perhaps 5 per cent of these tails was composed of turpentine materials. This is, however, a fairly satisfactory separation, since only 5 per cent of 32 per cent, or 1.6 per cent of the original crude, was not properly separated.

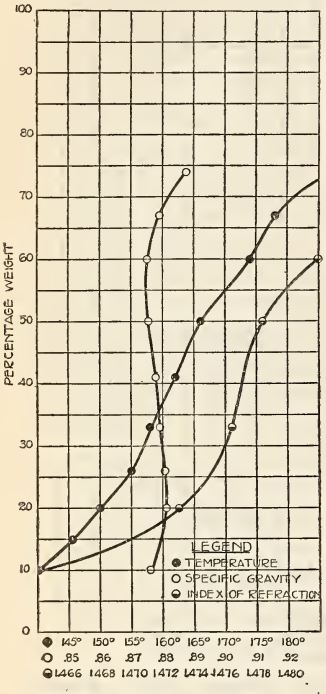

FIG. 30.—Boiling point, specific gravity, and index of refraction curves for crude turpentine No. 3, untreated.

REFINING OF CRUDE TURPENTINE NO. 3.

Crude turpentine No. 3 was obtained from a destructive distillation plant using "lightwood" as a raw material; the distillation process is very similar to that employed by the hardwood retort plants in the North, the horizontal cylindrical retorts holding about one cord of wood and the complete distillation taking only 24 hours. The total distillate is condensed and collected together and the pyroligneous acid removed from the crude oil by settling. The crude oil thus obtained is distilled with steam until nearly all the volatile oil is removed. The crude turpentine used in the refining experiments was a sample of the distillate obtained from this crude oil.

ANALYSIS AND CHEMICAL TREATMENT.

The analysis of the crude is shown in figure 30. It can be seen from the curves that this crude is a very complex mixture, since none of the properties remain at all constant over any considerable

portion of the distillation; a large part boils below the usual boiling point of turpentine, and the specific gravity over the complete range of the distillation is higher than any portion (except the residue) of a refined turpentine should be. All the fractions were also colored and had very disagreeable odors. It was seen that no separation by distillation alone could give a distillate suitable for a refined turpentine, and therefore it was necessary to give a chemical treatment before refining by distillation. The crude was therefore agitated with caustic soda solution at 55° C. until action ceased. The cessation of action is shown by treating a small amount of the crude with additional caustic soda at the same temperature without any resultant change in the color of the caustic solution.

The analysis of the crude treated in this manner is given in figure 31. The proportion of material boiling below 155° C. was decreased considerably, the specific gravity of all the fractions was decreased, and the color and odor of all fractions improved. The index of refraction curve was, however, somewhat irregular, and all the fractions still retained some disagreeable odor. That portion of the distillate between 11 per cent and 64 per cent was more suitable for a refined turpentine than that above or below, and it was therefore decided to separate the treated crude into 11 per cent heads. 53 per cent hearts, and 36 per cent tails.

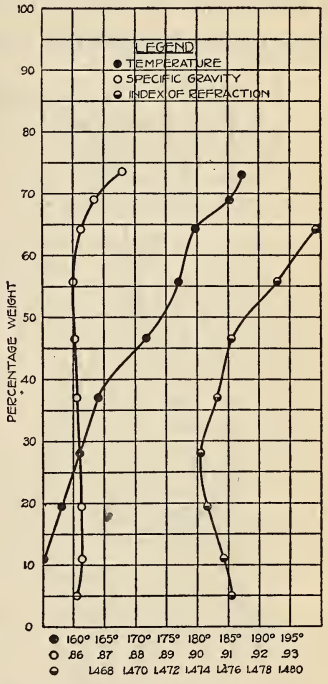

FIG. 31.—Boiling point, specific gravity, and index of refraction curves for crude turpentine No. 3, after treatment with caustic soda solution.

DISTILLATION.

The crude was run into the still at a speed of 25 gallons per hour, and the speeds of the heads and hearts were maintained respectively, as nearly as possible, at 11 per cent of 25, or 2.75 gallons per hour, and 53 per cent of 25, or 10.75 gallons per hour. During this distillation great difficulty was experienced in regulating the speed of the products, and the effects of this are seen in the composition of the products.

PRODUCTS.

The analyses of the products are shown in figures 32, 33, and 34.

HEADS.

The heads (fig. 32) contained about 80 per cent of material of complex composition, with widely varying boiling points and indices of refraction; the color of this 80 per cent was darker and the odor much more disagreeable than those of the last 20 per cent. The

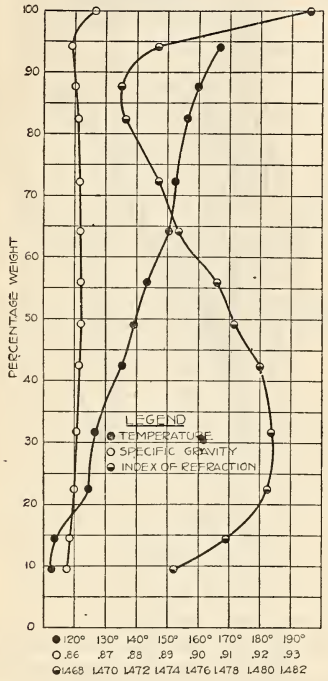

FIG. 32.—Boiling point, specific gravity, and index of refraction curves for "heads" obtained in refining of crude turpentine No. 3.

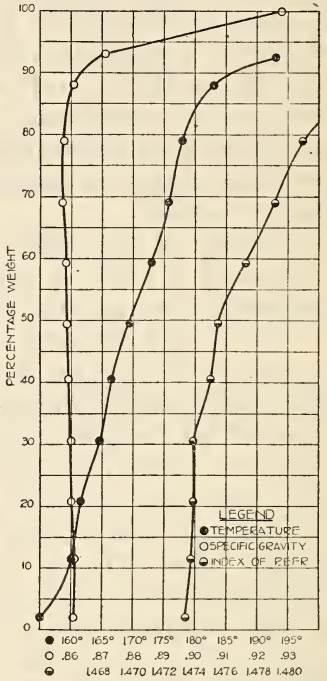

FIG. 33.—Boiling point, specific gravity, and index of refraction curves for "hearts" obtained in refining of crude turpentine No 3.

properties of this last 20 per cent were such that it could well be included in the hearts—that is, the separation of heads from hearts was not complete.

HEARTS.

The specific gravity and index of refraction of the first fraction of the hearts (fig. 33), indicated that the separation of the heads from the hearts was complete, but the boiling point, the odor and color of this first fraction indicated that a small amount of heads material was present in the hearts. It is probable that this incomplete separation

between the heads and hearts was largely due to the variation in the speed of the heads; this speed varied from 3.1 to 2.3 gallons per hour, and while the heads were running at 3.1 gallons per hour, some hearts material would be distilled over with the heads; when the speed dropped to 2.3 gallons per hour some heads material would escape in the returns from column A_1 to column A_2 and thus get into the hearts. The hearts also contained probably more heavy material with boiling points above 180° C. than is desirable in a well-refined turpentine.

TAILS.

The tails (fig. 34) contain about 5 to 6 per cent of hearts material showing an incomplete separation of hearts from tails.

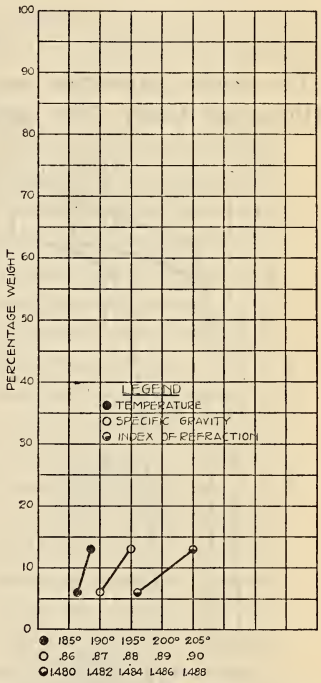

FIG. 34.—Boiling point, specific gravity, and index of refraction curves for "tails" obtained in refining of crude turpentine No. 3.

REFINING OF CRUDE TURPENTINE NO. 4.

The turpentine plant from which crude turpentine No. 4 was obtained is operated in connection with a sawmill cutting longleaf pine almost exclusively. The raw material for the distillation consists of the sawdust together with the waste slabs, edgings, and trimmings, the large-sized materieal being "hogged" or made into chips before it is conveyed to the turpentine plant. The steam distillation process is used, the maximum pressure in the retorts being 10 pounds.

ANALYSIS.

The analysis of this crude turpentine is given in figure 35. This crude is of simple composition in comparison with Nos. 1, 2, and 3, being composed of about 84 per cent of turpentine and 16 per cent pine oil, with no evidences of the presence of any dipentene, or of any heads, except that the odor of the first fraction was somewhat different from that of the next few fractions.

It was desired to obtain one refined steam distilled turpentine containing comparatively large amounts of pine oil in order that the technical properties of two turpentines similar in composition, except

for the proportion of pine oil present, might be compared. It was decided therefore to separate this crude into about 2 per cent heads, 88 per cent hearts, and 10 per cent tails, and thus obtain a refined turpentine with more heavy oils than No. 2, the other steam distilled turpentine which was refined.

DISTILLATION.

The crude turpentine was run into the still at the rate of 24.8 gallons per hour. The speed of the heads varied from 0.2 to 1.0

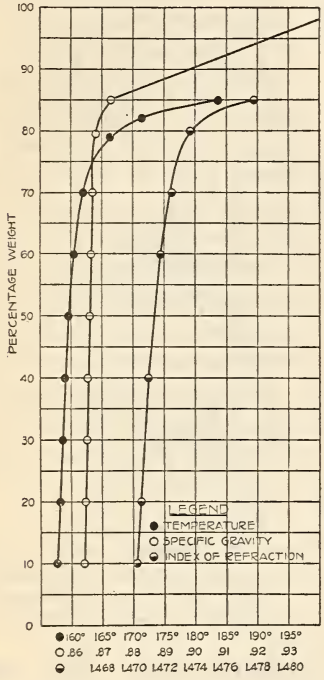

FIG. 35.—Boiling point, specific gravity, and index of refraction curves for crude turpentine No. 4.

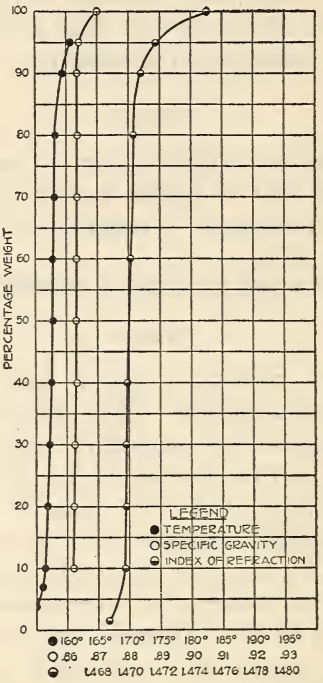

FIG. 36.—Boiling point, specific gravity, and index of refraction curves for "heads" obtained in refining of crude turpentine No. 4.

gallon per hour with an average of about 0.5 gallon per hour, and the hearts varied from 20 to 23 gallons per hour with an average of about 21.7 gallons per hour.

PRODUCTS.

HEADS.

The analysis of the heads from this run (fig. 36) showed the presence of only a very small amount of material that differed from the main portion of the turpentine. The first fraction of 1.5 per cent had a slightly lower index of refraction than any of the rest, and the

odor of the first 10 per cent of the distillate was quite different from the remainder. As in the case of crude turpentine No. 2, the amount of this material is so small, and its properties are so slightly different that it is unnecessary to attempt to separate it.

HEARTS.

The analysis of the hearts (fig. 37) showed about 6.5 per cent of pine oil present as was to be expected from the manner of regulating the distillation.

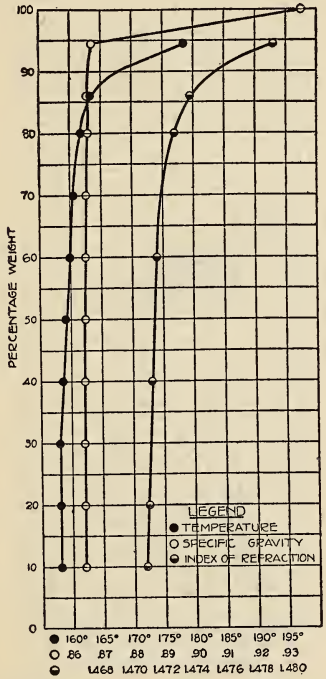

FIG. 37.—Boiling point, specific gravity, and index of refraction curves for "hearts" obtained in refining of crude turpentine No. 4.

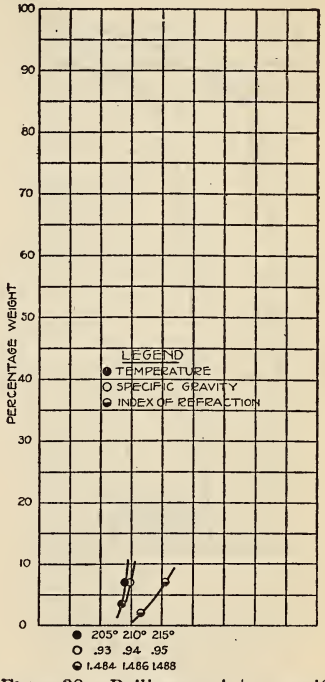

FIG. 38.—Boiling point, specific gravity, and index of refraction curves for "tails" obtained in refining of crude turpentine No. 4.

TAILS.

The tails (fig. 38) were apparently entirely free from hearts material, the very high values for the physical properties of the first fraction, 6.5 per cent, indicating that only a very small proportion of this fraction could possibly be made up of turpentine material. The separation in this case is therefore very satisfactory, since the hearts contain probably no more heavy material than is allowable in a good grade of turpentine, and the tails are practically free from turpentine.

PRODUCTS OBTAINED BY COMMERCIAL REFINING.

In order to obtain a comparison between the efficiency (as regards completeness of separation) of the column still, which was used in

this investigation, and that of the ordinary pot still commonly used in commercial practice, samples of the turpentine and pine oil, refined at the plant where this crude turpentine was produced, were obtained and analyzed. The samples were both from the same charge of crude and were refined by a single distillation with steam. The turpentine (fig. 39) is seen to contain about 12 per cent of heavy oils, while the pine oil (fig. 40) contains about 30 per cent of turpentine, showing that a very incomplete separation was obtained.

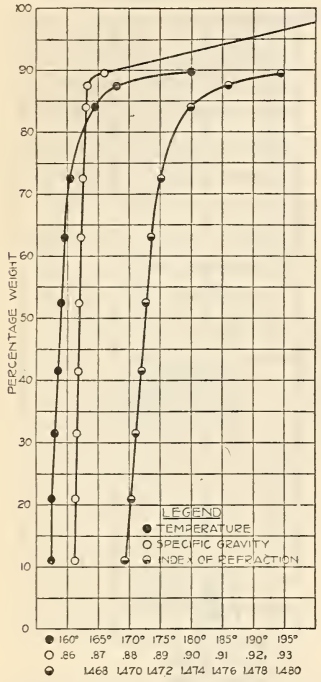

FIG. 39.—Boiling point, specific gravity, and index of refraction curves for a commercial wood turpentine (crude No. 4) refined in an ordinary pot still.

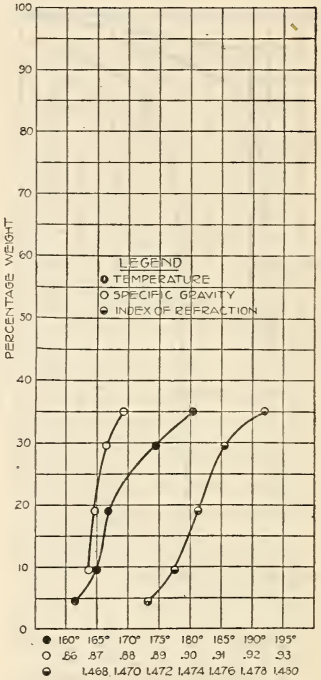

FIG. 40.—Boiling point, specific gravity, and index of refraction curves for commercial pine oil refined in an ordinary pot still.

REFINING OF CRUDE TURPENTINE NO. 5.

Crude turpentine No. 5 was produced from "lightwood" by means of the bath process of distillation. The "lightwood" in cordwood form is loaded on cars and these are run into large horizontal cylindrical retorts; then the hot bath material, pine-tar pitch, is circulated through the retort, the "extractor" and the furnaces in the order given. In the furnaces the temperature of the bath material is kept up to a maximum of 195° C. Live steam is blown through the bath in the extractor to remove the volatile oils which are carried by the bath from the retort. These volatile oils constitute the crude turpentine used in the refining experiments.

ANALYSIS.

The analysis of this crude turpentine is given in figure 41. There was no evidence of any heads material in this crude, except that there was a slightly different odor in the first fraction, and apparently about 57 or 58 per cent could be obtained which would contain a very small amount of heavy oils. It was decided, therefore, to attempt to separate the crude into the smallest possible quantity—2 per cent—of heads, 55 per cent of hearts, and the rest tails.

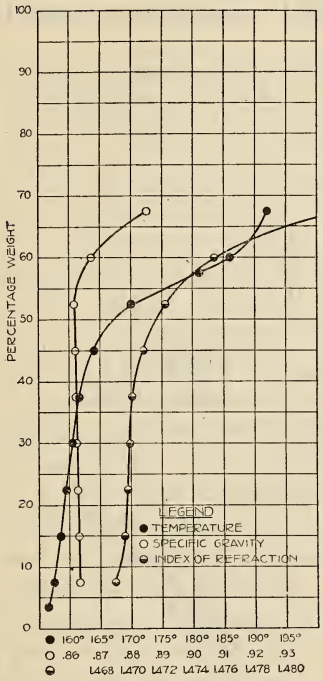

FIG. 41.—Boiling point, specific gravity, and index of refraction curves for crude turpentine No. 5.

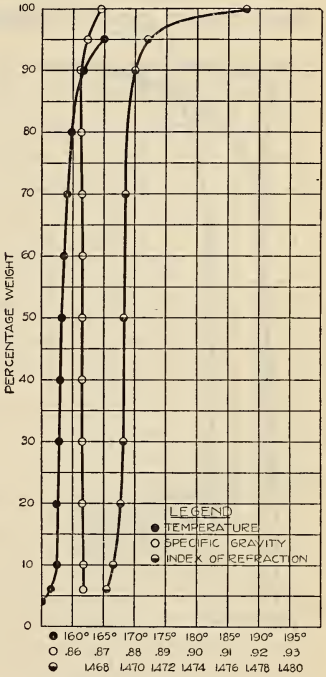

FIG. 42.—Boiling point, specific gravity, and index of refraction curves for "heads" obtained in refining of crude turpentine No. 5.

DISTILLATION.

The crude was run into the still at the rate of 25 gallons per hour, and the steam and water were adjusted to give as nearly as possible 0.5 gallon per hour of heads and 13.75 gallons per hour of hearts; these adjustments were maintained within the usual limits of variation.

PRODUCTS.

HEADS.

The analysis of the heads thus obtained is given in figure 42. From the boiling point and index of refraction curves it is apparent that

the first 10 per cent of the distillate contains a small amount of material with properties somewhat different from the rest of the distillate, and this was further indicated by the odor of the first fractions. As with turpentines No. 2 and No. 4, however, it is probable that there is so little of this material present that it is not only impracticable but unnecessary to attempt its separation.

HEARTS.

The hearts (fig. 43) are seen to be almost free from heavy oils, only about 2 per cent of material with a gravity of 0.890 being

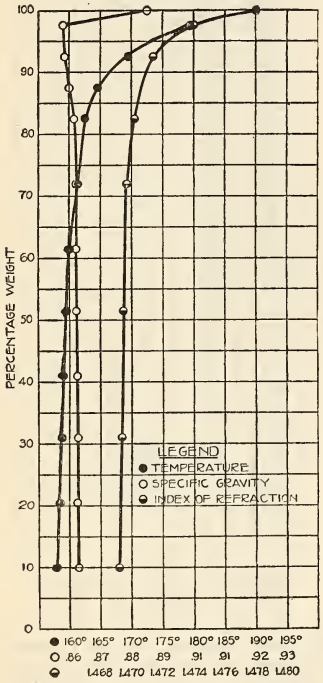

FIG. 43.—Boiling point, specific gravity, and index of refraction curves for "hearts" obtained in refining of crude turpentine No. 5.

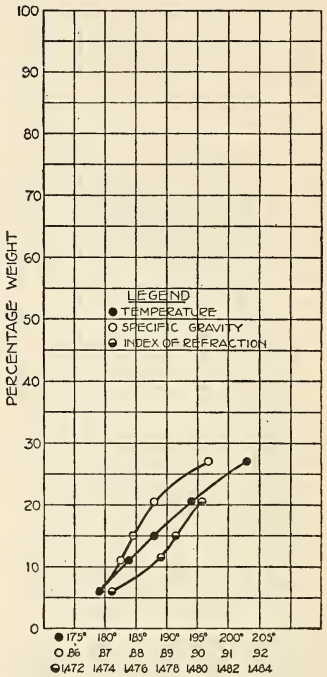

FIG. 44.—Boiling point, specific gravity, and index of refraction curves for "tails" obtained in refining of crude turpentine No. 5.

present, and the low gravity and index of the residue indicating that even this 2 per cent is largely composed of substances similar to the last few fractions of the distillate. A very nearly complete separation of hearts free from tails was therefore accomplished in this run.

TAILS.

The tails, however, are seen (fig. 44) to contain probably 15 per cent of hearts material, so that the separation of tails free from hearts was not complete.

REFINING ON A COMMERCIAL SCALE.

The refinings of the five crude turpentines were intended not only as experiments in refining, but also as studies of the composition of crude wood turpentines and the products obtainable from them. Especially, they proved to be a means of obtaining samples of wood turpentine with known compositions and methods of production, so that these samples might be used in comparative tests to determine the industrial value of wood turpentines of different composition. There was no aim to secure ideal conditions for the different distillations; throughout the experiments the arrangement of the still was not changed, and only in two cases were the distillations repeated in order to secure more accurate results. Hence, it must not be thought that, in all cases, the best results were obtained, or that the column was most suitably arranged. The composition of crude turpentines 2, 4, and 5, for instance, was such that it was not necessary to separate the constituents with boiling points below those of refined turpentine; instead, it would have been preferable to produce a refined turpentine and a refined pine oil, but the arrangement of the column was not suited to the production of these, and in no case was a refined pine oil produced.

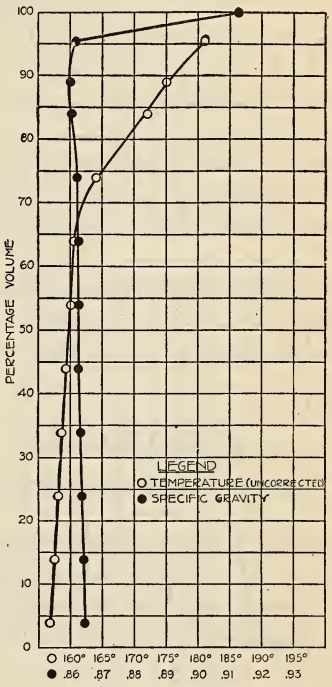

FIG. 45.—Boiling point and specific gravity curves for turpentine obtained in commercial refining of crude turpentine No. 5.

However, in another piece of work under conditions more nearly commercial, the column was arranged for the production of a refined pine oil as well as a turpentine.

FIELD WORK ON A CRUDE TURPENTINE.

In this case the still was set up at the plant where crude turpentine No. 5 was produced. The arrangement of the still was similar to that in the experimental work, except that the crude reservoir was modified for continuous long runs, and the grouping of the sections was changed so that the upper column, A_1, contained 13 boiling cap sections and 3 reflux condenser sections, while the lower column, A_2, contained only 5 boiling cap sections and 2 reflux condenser sections. The refined turpentine was distilled from A_1 and

the refined pine oil from A_2. (See fig. 20.) The analyses of the products obtained from one run, as shown in figures 45 and 46, give a good idea of the separations obtained under these conditions. The turpentine contained about 4 per cent pine oil, and the pine oil contained about 2 per cent turpentine.[1] This seemed to be the most complete separation possible, since with larger proportions of pine oil in the turpentine the amount of turpentine in the pine oil decreased, and vice versa.

Another interesting result was obtained in the test for determining the proper control of the distillation, in which it was found that the control of the still could be secured through the specific gravity of the products rather than through an arbitrary speed. Where the specific gravities of the two constituents to be separated are different, the specific gravity gives a nice control; but with a crude turpentine, such as No. 3, where two products (heads and hearts) have nearly identical gravities this method is not applicable.

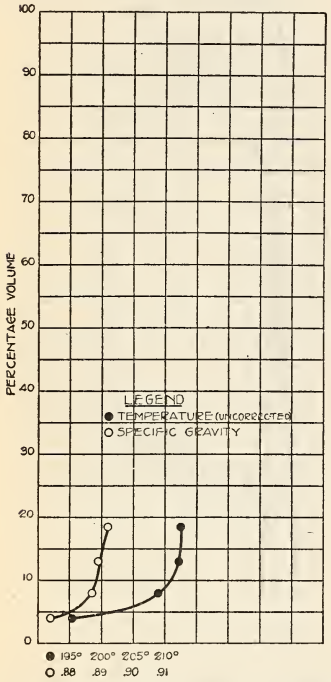

FIG. 46.—Boiling point and specific gravity curves for pine oil obtained in commercial refining of crude turpentine No. 5.

SUMMARY OF EXPERIMENTS.

The crude turpentines that were analyzed are sharply divided into two groups according to their compositions and to the methods used in their production. The means for their proper refining naturally follow the same grouping, which is as follows:

Group 1.—Includes crude turpentines 2, 4, and 5, which were produced at temperatures below 200° C.

Group 2.—Includes crude turpentines 1 and 3, which were produced at temperatures above 200 C.

[1] It will be noticed that figs. 45 and 46 are different in many ways from the preceding distillation curves. Index of refraction curves are not given, the boiling-point values are uncorrected, and the percentages are by volume and not by weight. These represent the results of analyses with portable apparatus, which can be set up and used without the conveniences of the chemical laboratory. Two 50 c. c. cylinders, graduated to 1 c. c., and one 500 c. c. measuring flask, take the place of the more delicate balances in determining the percentages of distillate, and the refractometer and barometer can be dispensed with; otherwise the method is the same. For many purposes this method is sufficient; but for close, careful work, the refinements described on pages 11–13 are necessary.

The following conclusions have been reached for the refining of crude wood turpentines like those of group 1:

(1) A fractional distillation without chemical treatment is sufficient for the production of good grades of turpentine and pine oil.

(2) The separation of light oils with boiling points lower than those of the turpentine is unnecessary.

(3) Better separation of the turpentine from the pine oil, or, in other words, a greater purity of the final products is obtained with a column still than with an ordinary pot still.

In the refining of crude wood turpentines like those of group 2 the following conclusions apply:

(1) A chemical treatment is required before a distillation can produce a good grade of refined turpentine.

(2) The color and odor of the refined turpentine obtained from the chemically treated crudes by distillation are much improved by the separation of the "light oils" with boiling points lower than those of the turpentine.

(3) Although no data are given to show what results might be obtained in an attempt to separate the "light oils" by distillation in an ordinary pot still, yet it is probable that these light oils could not be successfully separated.

COMPOSITION OF WOOD TURPENTINES.

THE RELATION BETWEEN PRODUCTION AND COMPOSITION.

If the crude turpentines are arranged according to the maximum temperatures of their production, the order would be 4, 2, 5, 1, and 3. The proportion of dipentene in the refined turpentines prepared from these crudes increases in the same order as the maximum temperatures of production. (See figs. 37, 38, 43, 14, and 33.) There would have been a more proper comparison between maximum temperatures and proportion of dipentene in the crude, rather than in the refined, turpentines, but the analyses of the crude turpentines do not in all cases indicate the proportion of dipentene present, as, for instance, in crude turpentines 1 and 3. (Figs. 21 and 30.)

As was to be expected, there is also a relation between maximum temperatures and the amount of "light oils" (with boiling points below 157° C.); for example, in crude turpentines 1 and 3, produced at (unknown) higher temperatures, light oils are present.

A similar relation holds between the maximum temperatures of production and the quantity of the products removable by treatment with caustic soda.

These relations between composition and temperature of production are given in Table 2.

TABLE 2.—*Relation between temperature of production and composition of crude wood turpentines.*

Crude turpentine.	Maximum temperature of production.	Dipentene in refined turpentine.	Light oils, boiling point below 157° C., insoluble in NaOH.	Oils, soluble in NaOH.
No.	*° C.*	*Per cent.*	*Per cent.*	
4	116	Practically none.[1]	None.	None.
2	148	About 10.	None.	None.
5	195	About 15.	None.	None.
1	High.	About 25.	About 3.	Some.
3	Higher.	About 40.	About 11.	More.

[1] For a more plausible reason than difference in temperature for the smaller amount of dipentene in turpentine No. 4, see page 53.

COMPARISON WITH GUM TURPENTINES.

A study of the variations in composition of gum turpentines just completed at the Forest Products Laboratory indicates that the volatile oil freshly distilled from oleoresin obtained by chipping live trees of longleaf pine contains only very small amounts of heavy oils (with gravity above 0.875). Therefore the 5 per cent of heavy oil shown in figure 2 is probably due to a partial oxidation of the terpenes in the original freshly distilled oil. Except for the presence of these heavy oils, figure 2 represents the composition of a typical gum turpentine, though in some the range of the values for the physical properties of the fractions might be slightly lower; in others, slightly higher.

HEAVY OILS.

On the other hand, the volatile oil obtained by the distillation of pitchy longleaf pine contains considerable quantities of heavy oils, and their presence in refined wood turpentines may result from incomplete separations of heavy oil from turpentine, even with an efficient column still. Still less perfect separations can be made with the pot stills commonly used, and there is a natural tendency on the part of the refiner to increase the quantity of refined turpentine by increasing the proportion of heavy oils in the refined product.

The usual presence of heavy oils in wood turpentines and their usual absence in gum turpentines is, then, the first difference between the two. Even in an old gum turpentine which contains heavy oils (like fig. 2), it is probable that the composition of these heavy oils is different from those in wood turpentines (see Composition of heavy oils, p. 58).

DIPENTENE.

The presence of dipentene in wood turpentines and its absence in gum turpentines is another difference. The refined turpentines ob-

tained from four of the five samples of crude contained dipentene; it is probable that most wood turpentines will contain appreciable amounts of this substance. In some 75 samples of gum turpentine which have been examined in the Forest Products Laboratory no dipentene has been detected by the method of analysis used. It appears that the presence of dipentene in wood turpentine is not entirely due to the temperature to which the turpentine is subjected, because most gum turpentines have been subjected to temperatures of at least 150° C. during their distillation, and yet crude turpentine No. 2, which was produced at 50 pounds steam pressure (148° C.), contained considerable quantities of dipentene. Dipentene was also found in the volatile oil distilled from lightwood by steam at atmospheric pressure.[1] The influence of temperature is indicated by the increased amounts of dipentene in wood turpentines produced at high temperatures. The dipentene in wood turpentine may, then, come from two sources, (1) from the dipentene present in the volatile oil as contained in the wood, and (2) from the transformation of some of the pinene into dipentene by the high temperatures used in the distillation.[2]

LIGHT OILS.

The presence of light oils in the wood turpentines produced at higher temperatures is the third possible difference. A crude turpentine containing light oils may be so refined that the product will be free from light oils (as in the case of crude No. 1), but the separation is difficult and can not readily be made without some kind of a fractionating column. If light oils are present in the crude turpentine small quantities are likely to be in the refined turpentine.

ROSIN OILS.

The fourth possible difference between wood and gum turpentines is difficult to describe, since it does not greatly affect the physical properties expressed in the distillation curves. For instance, in the analysis of refined turpentine No. 3 (fig. 33) it was quite noticeable that the odor and color of all the fractions differed from similar fractions of other turpentines. Except for the small amount of light oils present (see p. 42) the peculiar odor and color apparently did not tend to concentrate either in the first or last fractions, but were distributed rather evenly throughout the distillate. These properties

[1] "The Distillation of Resinous Wood by Saturated Steam," Bulletin 109, Forest Service.

[2] The absence of noticeable amounts of dipentene in turpentine No. 4 may be explained from its source—green sawmill waste; that is, old, dead, lightwood or stumps may contain dipentene while green freshly cut timber may not. It is expected that these debatable points will be settled by some work now under way in the Forest Products Laboratory.

were therefore probably due to the presence of some materials other than terpenes, with boiling point, gravity, and index of refraction not much different from the terpenes; the only strong indication of the presence of materials other than terpenes was in the high index of refraction of the first 30 per cent. From the method of production of this turpentine, these other materials can only be high-temperature decomposition products of wood fiber or of rosin. Decomposition products of wood fiber could not be present in very appreciable proportion, because the oils from this source, which would be insoluble in caustic soda, with boiling points 155° to 180°, and gravity in the vicinity of 0.85 to 0.87, are extremely small in amount. The destructive distillation of rosin, however, will yield yellow oils answering these requirements; the odor of these rosin oils (rosin spirits, rosin naphtha) is very similar to the fractions of this destructively distilled wood turpentine, and it is likely that the peculiar odor and color of destructive wood turpentines are due largely to the presence of "rosin spirits."

These comparisons of composition show that most wood turpentines will be sufficiently different in composition from gum turpentines, so that the method of analysis used in these investigations will readily distinguish between them; a wood turpentine produced from green timber at such low temperatures that no dipentene is formed and so refined that no heavy oils are present is, however, very similar to a gum turpentine; that is, the terpenes present in the wood from freshly cut long-leaf pine are very similar to the terpenes in the oleoresin obtained by chipping the live tree. The boiling point, the specific gravity, and the index of refraction curves from the two turpentines do not differ greatly, but these properties seem to be slightly lower in the fractions from the wood turpentines (compare figs. 2 and 37). This difference is, however, not great enough to provide a sure means of distinguishing between the two kinds of turpentines, since a gum turpentine with low values might be almost the same as a wood turpentine with high values. It is probable, therefore, that the same constituents are present in each, but that more of the higher boiling and higher gravity terpenes are generally present in the gum turpentines.

ODOR.

There is a considerable difference in odor between the gum turpentines and the wood turpentines, even between those which are nearest alike in composition. In most cases, however, this difference in odor is not due to differences in the main constituents. For instance, in the refined turpentine from No. 4 the main constituents are probably the same as in the gum turpentine shown in figure 2, and yet there is a decided difference in the odor of these two turpentines. Even the

presence of dipentene does not fully account for the difference in odor between wood and gum turpentines. Refined turpentines 2 and 5, both of which contained considerable quantities of dipentene, resembled gum turpentine in odor more than the products from No. 4, which was more nearly like gum turpentine in composition. It seems likely, therefore, that the distinctive odor of many wood turpentines is due to some material which occurs in so small a quantity that its presence is not readily indicated in any other manner than by the odor. The odor of a wood turpentine like No. 3 is probably due to the presence of rosin spirits, as mentioned on page 53.

EFFECT OF COMPOSITION ON TECHNICAL PROPERTIES.

The most valued properties of turpentine are usually considered to be its volatility, its solvent power, and its "drying" properties.

VOLATILITY.

The volatility of wood turpentines as compared to gum turpentines would probably not be greatly affected by the differences in composition. This property is measured, approximately, by the range of boiling points of the various constituents. Large quantities of heavy oils decrease volatility, but it is doubtful whether the effect of small quantities, up to 10 per cent, would be noticeable in practice.

SOLVENT PROPERTIES.

It is likely that the solvent properties of dipentene are quite similar to those of pinene, since these terpenes are so much alike in other respects; the solvent properties of the other materials which do not occur in gum turpentines, but which may be present in wood turpentine are probably sufficiently similar so that the small proportion of these which may be present does not appreciably affect the solvent properties of the mixture.

DRYING PROPERTIES.

In drying properties dipentene is apparently equal to pinene, since it has been found that the time required for drying a mixture of dipentene and linseed oil is the same as for drying a similar mixture of pinene and linseed oil.[1] In the case of the drying properties it is not likely that small amounts of rosin spirits, light oils, or even heavy oils, would greatly affect the industrial value of the turpentine. Until further data are available on the relation between the composition and industrial value of turpentines, the differences in composition between wood and gum turpentine should not be considered as necessary indications of corresponding differences in value.

[1] This was determined by Edward Kremers, of the University of Wisconsin, in an investigation of terpenes as oxygen conveyors.

CHANGES IN COMPOSITION AFTER REFINING.

The analyses of refined turpentines were made within a few days after the refining. Afterwards these refined samples were kept for considerable periods, some in glass carboys, others in wooden barrels or iron drums, and further anlyses were made from time to time to determine any changes in composition. Since the methods of storage were not the same the results are not accurately comparable, though they indicate the kinds and amounts of change which may take place during storage.

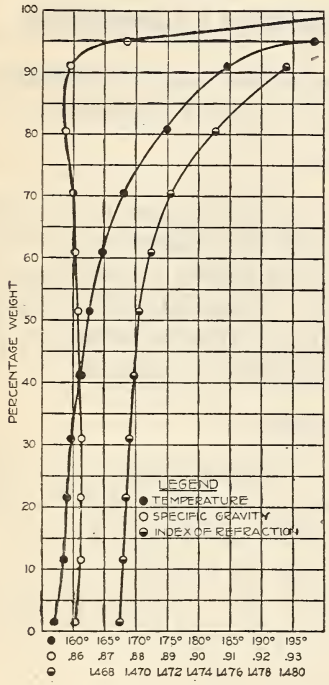

FIG. 47.—Boiling point, specific gravity, and index of refraction curves for the turpentine obtained from crude No. 1 analyzed after six months.

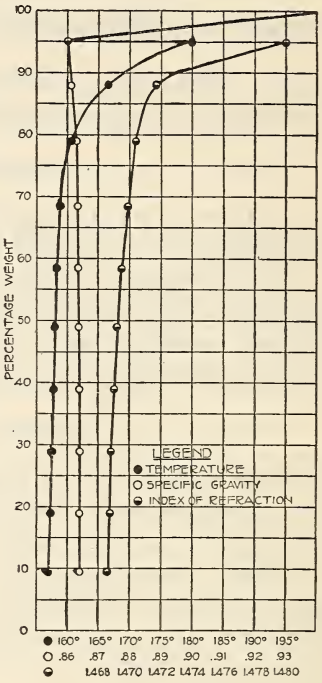

FIG. 48.—Boiling point, specific gravity, and index of refraction curves for the turpentine obtained from crude No. 2 analyzed after nine months.

Refined turpentine No. 1, the original analysis of which is shown in figure 24, was analyzed again after six months. (See fig. 47.) The only change which had taken place in this time was an increase in the amount of heavy residue from about 6 to 10 per cent; the odor and color had not been appreciably affected.

Refined turpentine No. 2 (original analysis, fig. 28) was analyzed after nine months (fig. 48); during this period the heavy residue had increased from 3.5 per cent with a gravity of 0.885 to 5.5 per

cent with a gravity of 0.94. Otherwise the sample seemed to be unchanged; it was still colorless and with no appreciable change in odor.

Refined turpentine No. 3 (original analysis, fig. 33) was analyzed after a period of nine months (fig. 49); there were no indications of change in composition.

Refined turpentine No. 4 (fig. 37) was analyzed after nine months (fig. 50); no apparent change in composition had taken place.

Refined turpentine No. 5 (fig. 43) was analyzed after 3 months

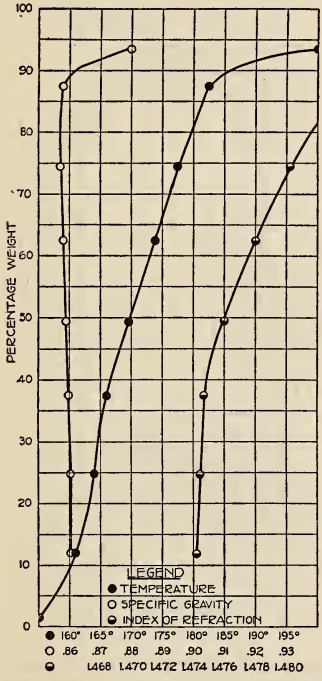

FIG. 49.—Boiling point, specific gravity, and index of refraction curves for the turpentine obtained from crude No. 3 analyzed after nine months.

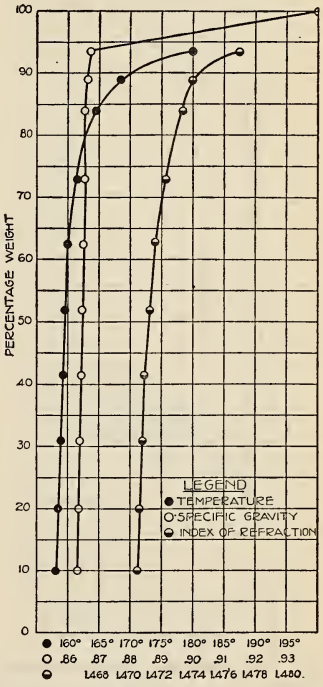

FIG. 50.—Boiling point, specific gravity, and index of refraction curves for the turpentine obtained from crude No. 4 analyzed after nine months.

(fig. 51); during this short time the amount of heavy residue had increased from 2 per cent with gravity of 0.885 to 4 per cent with gravity of 0.92. Other analyses, made after 6 and 10 months (figs. 52 and 53), showed a gradual increase in the amount of heavy residue. At the time of the last analysis a considerable yellow color had developed in this sample, possibly from the natural process of "aging," but more likely by contamination from an incompletely cleaned iron drum in which it was stored during a part of the time. In order to remove this color and also part of the heavy residue, the sample was

redistilled with steam in a small laboratory still without a fractionating column; the composition of the redistilled turpentine is shown in figure 54.

COMPOSITION OF HEAVY OILS IN WOOD TURPENTINES.

The presence of considerable quantities of heavy oils in the crude wood turpentines produced by steam distillation (see analyses of crude turpentines Nos. 2 and 4, figs. 26 and 35) indicates that some

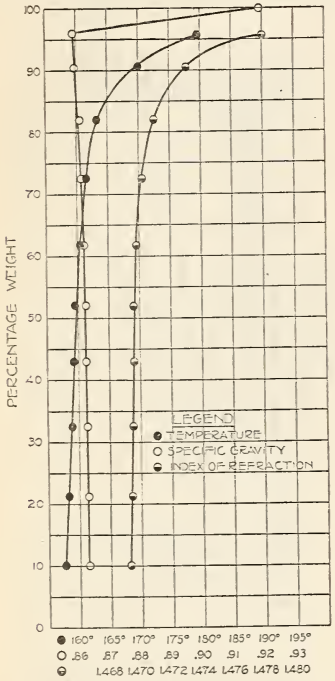

FIG. 51.—Boiling point, specific gravity, and index of refraction curves for the turpentine obtained from crude No. 4 analyzed after three months.

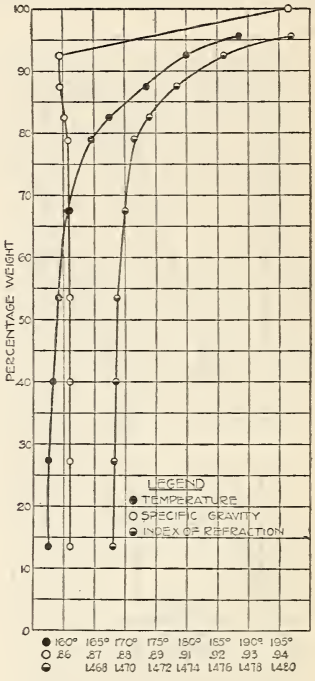

FIG. 52.—Boiling point, specific gravity, and index of refraction curves for the turpentine obtained from crude No. 5 analyzed after six months.

heavy oils, as such, are present in the wood itself, and are not formed during the distillation process. Experiments on steam distillation of longleaf pine have further confirmed these indications, since it was found that the proportion of heavy oil in the crude turpentine did not seem to be directly influenced by the temperatures of the distillation.

In the usual commercial refining practice these heavy oils are distilled over after the turpentine, and are marketed without further treatment as "pine oil." It was probably a sample of this pine oil

which was examined by Schimmel & Co.,[1] who identified the following bodies:

α-pinene, β-pinene (nopinene), camphene, limonene, dipentene, cineol, fenchyl alcohol, camphor, borneol, methyl chavicol, and α-terpineol. The first six of these, because of their low boiling points (all below 177° C.), are to be considered as normal constituents of the refined turnpentine[2] which, however, occurred in the "pine oil" on account of incomplete separation in the refining.

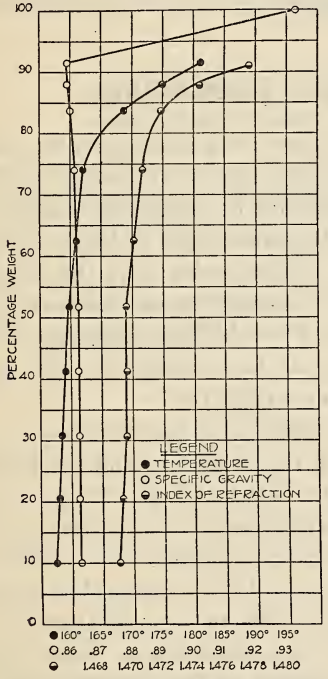

FIG. 53.—Boiling point, specific gravity, and index of refraction curves for the turpentine obtained from crude No. 5 analyzed after 10 months.

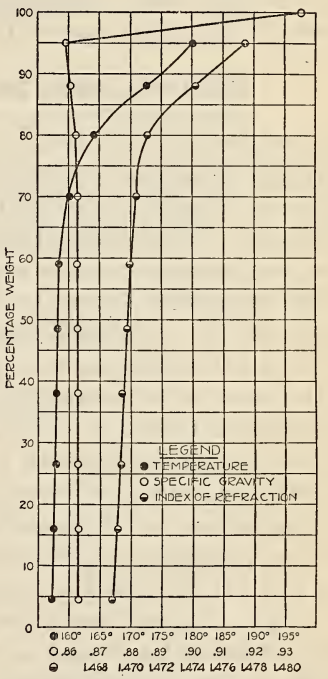

FIG. 54.—Boiling point, specific gravity, and index of refraction curves for turpentine obtained from crude No. 5 after redistillation.

The last five constituents have boiling points above 200° C. and may be considered as normal constituents of "pine oil" although,

[1] Semiannual Reports, Schimmel & Co., April, 1910, p. 100.

[2] With the exception of limonene and cineol, these low boiling constituents have been indicated as probable constituents of wood turpentine by the distillation curves. Because of the similarity between the two substances limonene could not be distinguished from dipentine by its effect on the distillation curves. Therefore limonene might have been present in any of the wood turpentines which contained dipentene. Cineol, however, has a considerably higher gravity (0.930) and a lower index of refraction (1.458) than dipentine and a boiling point (176° to 177° C.) which is near enough to that of dipentene so that the two would occur in the same fractions. It is possible, therefore, that very large quantities of cineol could not have been present in those turpentines whose distillation curves show a decreasing gravity and increasing index of refraction between 170° and 180°.

of course, small amounts of these substances may be present in the refined wood turpentine. (See p. 52.)

Since none of these five substances is known to be produced by the rapid oxidation of pinene or of the other terpenes in turpentine it is probable that the composition of the heavy oils in a wood turpentine (due to incomplete separation in refining) is not the same as those in a gum turpentine (produced by atmospheric oxidation). (See p. 52.)

The heavy oils in destructively distilled wood turpentines probably consist of these same materials, together with some decomposition products of the rosin (rosin oils).

SPECIFICATIONS FOR WOOD TURPENTINES.

The comparisons show that specifications for gum turpentine, based on physical properties, would not be applicable to all classes of wood turpentine. Especially would the presence of dipentene make such specifications inapplicable, because dipentene has a lower specific gravity and at the same time a higher boiling point than the terpenes in a gum turpentine. Also it might be desirable to include wood turpentines which contain small amounts of low boiling material (No. 3, fig. 33); such turpentines would certainly be excluded by any specifications based on the properties of gum turpentine.

It is apparent that, in drawing up turpentine specifications, these variations in composition must be taken into account; and the method of examination should differentiate (1) between high boiling points due to dipentene, and high boiling points due to heavy oils; (2) between low gravity due to dipentene and low gravity due to adulterations; and (3) between low boiling points due to incomplete separation of light oils, and low boiling points due to the addition of substances not normally present in crude wood turpentines. Such specifications can not be definitely recommended at the present time, because there is not sufficient information available on the technical value of wood turpentines of various compositions. Meanwhile, however, the method of analysis which is here presented will be of value in determining the composition of wood turpentines, and the various distillation curves will furnish, for comparisons, an idea of the variations possible in authentic wood turpentines.

APPENDIX.

PRACTICAL TESTS ON WOOD TURPENTINES.

Samples of each of the five wood turpentines, the refining of which is discussed in this bulletin, were submitted for practical testing to the Paint Manufacturers' Association and to several manufacturers of paints and varnishes. In these tests the sample turpentines were given the same numbers as the crudes from which they were distilled. The sample numbers and the numbers of the corresponding text figures, which show the composition of the turpentines at the time they were sent out for test, are as follows:

Turpentine No.	Figure showing composition.	
	No.	Page.
1	47	56
2	48	56
3	49	57
4	50	57
5	54	59

The reports of the tests are given in full, as submitted by the various cooperators. There is no detailed analysis of the reports for the purpose of drawing conclusions in regard to the use of these turpentines in the paint and varnish industries. These can best be drawn by those thoroughly familiar with the requirements of these industries. However, the following significant facts are apparent:

(1) The lack of concordance between the reports shows the futility of attempting to establish a general relation between the composition and the industrial value of turpentines, without standard methods for determining the industrial value. The various individual reports probably indicate very accurately the relative industrial values of the different turpentines so far as the particular company making the report is concerned, but no general relation is established.

(2) Aside from the odor, the wood turpentines do not seem to vary much from each other or from gum turpentine; at least, the differences between the several turpentines, as indicated in any one report, are not greater than the differences reported for the same sample by different manufacturers.

(3) Although the odor is the property most emphasized, there is no unanimity of opinion as to the comparative odors of the different samples; in most cases

the objection is that the odor is different from gum turpentines rather than that it is inherently objectionable.

The reports follow:

REPORT 1.

Referring to the samples of turpentine which you sent us October 24, we have completed the preliminary investigation, and in carrying through the tests, which were made comparatively, we have added to the five samples submitted by you a sample of regular standard gum turpentine, marked A, and a sample of our standard wood turpentine which we are regularly using, marked B. We found the specific gravities to be as follows:

A, 0.8680.
No. 4, 0.8680.
B, 0.8650.
No. 3, 0.8650.
No. 1, 0.8650.
No. 2, 0.8635.
No. 5, 0.8625.

Flash point:

A and B, not taken.
No. 3, 113° F.
No. 1, 109.4° F.
No. 5, 105° F.
No. 4, 103.6° F.
No. 2, 101.8° F.

Staining power (on white paper, least staining power ranked first):

No. 5, first.
A, second.
No. 3, third.
B, fourth.
No. 2, fifth.
No. 1, sixth.
No. 4, sixth.

Evaporation (on white paper, shortest time ranked first):

No. 5, first.
A, second.
No. 2, second.
B, fourth.
No. 3, fourth.
No. 1, fourth.
No. 4, seventh.

Odor:

No. 5 and A, equal.
Nos. 1, 2, 4, and B, equal.
No. 3, objectionable odor and color.

When used for varnish reducing and carefully watched, we were unable to note any perceptible difference, either in setting or in completed drying after 24 hours. What we considered the most delicate test in practical use was in using them for thinning quick-drying black, and the results here were as follows (the time given is in minutes and represents the time when the black had dried sufficiently hard to be varnished over without rubbing up):

A	50 minutes.
B, 1, 2, 5	90 minutes.
3 and 4	105 minutes.

After six days the quick-drying black which had been thinned with these various turpentines was examined, and we found that a sample thinned with A showed little or no tendency to thicken up; No. 5 thickened slightly; and the balance had all thickened quite a little, but showed practically no differences.

In general way I would say that it is our judgment that for the general purposes for which material of this kind is used odor is the most important

feature, inasmuch as unfortunate odor has been the greatest objection to a large use of this class of material in the past, and at the present time it is the main cause of the prejudice against it.

From the standpoint of working qualities there is, as you will note, quite a decided action in slowing up the drying. I am not aware as to just what causes this, and of course for many purposes it would not be serious. There are many uses, however, for quick-drying color where the time requirements are so imperative that none of these materials could be used. We do not understand why the same measure of influence on the drying does not show up in connection with varnishes, but as a matter of fact it does not.

We should say that your sample No. 5 is decidedly better in general characteristics than any wood turpentine we have ever seen. In every point, excepting the drying in quick-drying black, it shows up entirely equal to straight turpentine.

Nos. 1, 2, 4 are satisfactory as wood turpentines, and would be usable for all purposes for which high-grade wood turpentine is at the present time usable.

The sample tested under B represents wood turpentine, of which we have used a considerable quantity and with which we have had practically no trouble excepting from the standpoint of odor.

It is impossible at the present time to substitute wood turpentine for a pure spirits in many places on account of the stronger odor, and from his standpoint your sample No. 5 looks particularly interesting.[1]

Report 2.

Sample was taken from each can and compared in laboratory with pure gum spirits. The only objection raised was the decidedly objectionable odor in the No. 3 as well as the objectionable odor and slow evaporating in No. 5.

The samples were then tested as a thinner or solvent in an ordinary house paint and the same results obtained. The man applying the goods objected to the odor of both Nos. 3 and 5.

I then melted a batch of varnish and divided it into six equal parts, thinning five of these with the five samples of wood turpentine and the sixth part with pure gum spirits,[2] so that the body or base of all are identical.

After filtering and settling these six varnishes were submitted to practical tests by our head tester, who reports as follows:

Working with brush	Good.
Drying	Nos. 3 and 6 best. Nos. 1, 2, and 4 fair. No. 5 slow.

Color all up to standard. Odor: Nos. 3 and 5 strong odor; No. 3 most objectionable; Nos. 1, 2, and 4 fair; No. 6, sweet.

In having this test made we took great care both in making and testing the varnish. The man who tested did not know that he was not testing a regular run of six batches of one of our standard varnishes, which shows conclusively that he was doing his duty in an unbiased manner, and, as you will note, his report on odor corresponds with both laboratory report and test made by painter.

Report 3.

Material or subject.—Wood turpentine Nos. 2, 3, 4, and 5 from United States Department of Agriculture, Forest Products Laboratory.

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[1] The large variation in the drying properties found by the quick-drying black test indicated that this test offered a fairly simple method of determining the effect of the removal of the heavy oils on the drying properties. Small samples of each of the five turpentines were redistilled so as to prepare samples containing no heavy oils, and these special samples were submitted for the drying test. It was reported that the time of drying of all the samples had been brought closer together and closer to that of gum turpentine.

[2] Reported as No. 6.

Remarks.—For a comparative test with pure gum turpentine as to suitability for varnish making.

I. CHEMICAL TESTS.

	No. 2.	No. 3.	No. 4.	No. 5.	Gum turps.
Specific gravity	0.864	0.868	0.870	0.866	0.865
Residue on evaporation.....per cent	.64	2.60	.79	.67	[1].60
Iodine absorption, per cent	371.6	298.7	388.5	392.9	429

DISTILLATION TEST.

	Boiling point.				
	154° C.	155° C.	150° C.	153° C.	154° C.
165° C.....per cent	86	40	87	91	95
165° to 175° C., per cent	9	44	8	6	5
Over 175° C., per cent	5	16	5	3	.....
Total	100	100	100	100	100
Color	W. W.	Pale straw.	W. W.	Very pale straw.	
Odor	Best, mild.	Rank, penetrating.	Third, greasy.	Second, good but strong.	

[1] About.

II. *Varnish-making tests.*—Solvent power was tested by mixing 10 parts of each sample (also of gum turps.) with 1 part of a hard gum varnish. The pure turpentine precipitated the gum within one-half hour; No. 2 followed very shortly; then No. 5 (after about 6 hours). No. 4 held the varnish in solution, showing only a slight separation at the surface edges after a week; No. 3 held the varnish in solution perfectly for more than two months.

Other qualities were tested by reducing equal weights of the gum and oil from an agricultural varnish taken from the same batch, with equal volumes of the samples, as well as with pure turpentine, in such a way as to have all conditions as nearly as possible the same. The varnishes so made were not filtered, but were allowed to settle and age for three months. The percentage of volatile matter was then determined and the varnish was submitted to the usual tests of body, flowing, drying, brushing, etc.

The percentages of volatile matter were: For (I) varnish made with gum turps., 53.50; (II) No. 2, 54.87; (III) No. 3, 52.35; (IV) No. 4, 53.32; (V) No. 5, 54.10. The gum turp. varnish was the same in "body" as IV (as shown by the rate of rise oft he air bubble in a narrow test tube of the varnish); II and V were both slightly lighter in body, as would be expected from the higher percentage of volatile matter; but on the other hand III was still thinner, though showing less volatile. This fact is doubtless due to the much greater solvent power of turpentine No. 3, which results in a much less viscous solution.

Varnish IV showed the poorest flowing qualities; V was slightly better; I and II (in order) still better; and III much the best. The drying test shows that the varnishes with lighter body dry faster and harder, though II, in drying faster than III, shows an exception. The relative order is II first, III, V, IV, I. From a consideration of factors involved it is evident that if all were brought to the same body II, V, and VI would dry at about the same rate, followed by III and I.

In brushing qualities varnish I was ranked first, V next, III next, followed by IV and II. This ranking denotes the comparative ease with which a smooth, glossy film of proper thickness can be obtained upon a filled board.

The results of the tests may then be summarized as follows:

The samples are all stronger solvents than gum turpentine, No. 3 being the strongest; No. 2 and No. 5 only slightly better than the gum spirits. If odor could be disregarded, No. 3 would probably be in all respects the best substitute for gum spirits and would be an improvement on it in some ways; but

No. 3 is too disagreeable in smell to be used, except in small proportions. The choice therefore lies between No. 2 and No. 5, with the majority of points in favor of the latter.

Report 4.

VARNISH TESTS MADE WITH WOOD TURPENTINES SUBMITTED BY UNITED STATES FOREST PRODUCTS LABORATORY.

Two grades of varnish were made up from each of the wood turpentines—rubbing varnish and spar varnish. The formulas used throughout in making up these varnishes are as follows:

RUBBING VARNISH.

By measure.		By weight.	
Gums	21.4	Gums	27.97
Oils	19.4	Oils	18.62
Turpentine	59.2	Turpentine	53.26
		Driers	.15
Total	100.0	Total	100.00

SPAR VARNISH.

By measure.		By weight.	
Gums	16.4	Gums	20.17
Oils	42.3	Oils	41.5
Turpentine	41.3	Turpentine	38.2
		Driers	.13
Total	100.0	Total	100.00

In the manufacture of the varnishes it was noted that Nos. 2 and 4 had the best odor while Nos. 1, 3, and 5, under heat, gave off strong odors, somewhat irritating to the eyes. By heating up the various turpentines alone to 100° and observing the odor the same result was obtained.

The varnishes which were manufactured from these turpentines were applied to oak panels 6 inches wide 12 inches high and 1 inch thick. After the panels had been properly coated, they were subjected to a series of tests, and the data obtained from these tests are also recorded in the following charts.

EXTERIOR VARNISH.

No.	1	2	3	4	5.
Panel No.	I	II	III	IV	V.
Number of coats	3	3	3	3	3.
Odor	Fair; resembles gum turpentine but not quite as nutty; slight ethereal odor.	Excellent odor; as good as pure gum turpentine.	Extremely bad odor; resembles pyroligneous acid and acetone.	Fair; resembles turpentine.	Fair.
Action on eyes	None	None	Extremely irritating.	Very slight	None.
Ease of application	Easy	Drys quickly; easy; pulls when dry.	Easy	Easy	Easy.
General working character.	Easy; good	Easy; good	Easier than I or II.	Good	Easy.
Color density [1]	A	B	D	D	C.
Period of tackiness:					
A coat	3 hr. 30 min	3 hr. 30 min	2 hr. 50 min	2 hr. 55 min	2 hr. 55 min.
B coat	6 hr. 10 min	6 hr. 10 min	6 hr. 5 min	5 hr. 35 min	5 hr. 30 min.
C coat	6 hr. 00 min	5 hr. 45 min	5 hr. 35 min	5 hr. 10 min	5 hr. 15 min.
Period of hard drying.	Allowed 2 days between application of first and second coats. 4 days allowed between second and third coats.				
Body (rise of a bubble 2.5 cm. long in a tube 0.8 cm. diameter and 28 cm. long).	10 seconds (average of 3 trials).	11 seconds (4 trials).	7.6 seconds (3 trials).	10.7 seconds (7 trials).	11 seconds (4 trials).

[1] A, B, C, and D indicate degrees of darkness, A being darkest and D lightest.

RUBBING VARNISH.

No.	1.	2.	3.	4.	5.
Panel No.	VI.	VII.	VIII.	IX.	X.
Number of coats.	3.	3.	3.	3.	3.
Odor	Fair; resembles gum turpentine but not quite as nutty; slight ethereal odor.	Excellent odor; as good as pure gum turpentine.	Extremely bad odor; resembles pyroligneous acid and acetone.	Fair; resembles turpentine.	Fair.
Action on eyes	None	None	Extremely irritating.	Very slight	None.
Ease of application	Easy	Works easily at first but dries quickly and pulls on rubbing.	Very easy; does not dry readily under brush.	Harder to rub than VIII but easier than VII.	Same as No. 2
General working character.	Good	Good	Good	Good	Good.
Color density [1]	A	C	D	A	B.
Period of tackiness:					
A coat	1 hr. 35 min	1 hr. 35 min	1 hr. 20 min	1 hr. 30 min	1 hr. 20 min.
B coat	1 hr. 30 min	1 hr. 25 min	1 hr. 25 min	1 hr. 30 min	1 hr. 30 min.
C coat	2 hr. 30 min	2 hr. 25 min	2 hr. 20 min	2 hr. 15 min	2 hr. 10 min.
Period of hard drying.	Allowed 2 days before applying second coat. Allowed 4 days before applying third coat.				
Body (bubble 2.5 cm. long rises in tube 0.8 cm. diameter and 28 cm. long).	8 seconds (5 trials).	9.8 seconds (5 trials).	6.7 seconds (5 trials).	9.8 seconds (7 trials).	9 seconds (6 trials).

[1] A, B, C, and D indicate degrees of darkness, A being darkest and D lightest.

Temperature of laboratory during application of varnish: A coat, 90.5° F.; B coat, 93.2° F.; C coat, 86° F.

PAINT TESTS WITH WOOD TURPENTINES.

After the varnish test had been finished, the various turpentines were used to thin one standard paint formula, and this paint formula was applied to a series of panels to be placed on the southern test fence. The formula selected for the test consisted of 45 parts corroded white lead, 45 parts zinc oxide, 5 parts of asbestine, and 5 parts of whiting. This paint was divided into portions and thinned respectively with the five turpentines submitted for test. The paint formula itself was made up in condition resembling a ready mixed paint, as found upon the market, but containing nothing in the vehicle portion except linseed oil and drier. This formula was thinned in the proportion of 1 pint of turpentine to a gallon of paint for the priming coat, and one-half pint turpentine and one half gallon linseed oil for the second coat. The third coat was used without reduction. During the application of these paints the painter noted that No. 3 had a very objectionable odor, while Nos. 1, 2, and 4 had a very good odor, No. 2 probably being the best. In working and flatting properties, Nos. 1, 2, 4, and 5 gave the best results, and fully as good results as with the use of pure gum spirits. * * *

The evaporative values of these turpentines are satisfactory in every case, No. 3 evaporating more rapidly than the others, and none of them leaving any stain.

NOTE.—The panels painted with these test paints were exposed in September, 1910 (see Bulletin 30, Paint Manufacturers' Association), and the report of an inspection made in February, 1912, includes the following paragraph:

The panels which were painted with pigment formula 31 ground in pure linseed oil and reduced with various wood turpentines as thinners, indicated that the highest types of these materials were well suited to replace pure gum spirits of turpentine as a thinner for paints to be exposed out of doors. Wood turpentine No. 2 gave the whitest surface, while wood turpentine No. 5 gave the darkest.

REPORT 5.

No. 2: This is the best sample both in regard to odor and color and other qualities; it compares satisfactorily with gum spirits.

Nos. 4 and 5: These rank about the same from our point of view, being somewhat inferior to No. 2. No. 4 is lighter in color but No. 5 has less objectionable odor.

No. 1: This is next in quality to No. 4 and No. 5.

No. 3. This is the least desirable of the lot, having very disagreeable odor and being very dark in color. It also forms considerable residue when distilled with steam.

From a commercial point of view, we believe that No. 2 could be used to a considerable extent in the paint and varnish industries in place of gum spirits, but the odor of all the others would prevent their use except in a very small way.

Report 6.

(BY NAVY DEPARTMENT.)

(1) Tests have been concluded on four samples of wood turpentine (5 gallons each) submitted for testing purposes by the Director, United States Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wis.

(2) Results of physical tests:

The sample turpentines were marked Nos. 2, 3, 4, and 5, and were utilized in place of pure spirits of turpentine in four paints mixed according to the following formulas, each paint, being mixed with a different turpentine sample.

	Parts by weight.
White lead	9½
White zinc	5
Lampblack in oil	½
Raw linseed oil	3⅝
Test turpentine	½
Japan drier	¼

A similar number of paints (four) were mixed according to the above formula, using, however, pure spirits of turpentine instead of the test materials. These paints were considered as standards against which the paints containing the sample turpentines were to be tested. The paints were applied for the foregoing purpose to steel plates, and after the paints had dried the plates were exposed to the weather under date of October 12, 1911.

(3) It was noted that the paints containing the samples Nos. 2, 4, and 5 dried out in about the same time as the standard paints, while the No. 3 sample paint seemed to dry somewhat slower than the others. The plates were taken down for examination July 28, 1912, when it was found that the paints containing the sample turpentines were in excellent condition and quite equal to the standard paints in every respect.

(4) A second batch of paints were made up to practically the same formulas as previously used, with the exception that one half of the linseed oil was replaced with blown fish oil. These paints were applied on steel plates as before and were exposed October 16, 1911, to the weather in comparison to standard paints. These standard paints were mixed according to the same formula as the test turpentine paints, with the exception that pure spirits of turpentine was used. When examined July 29, 1912, it was found that all of the paints were in good condition, being about the same as the first batch of paints which were made up. It was noted that the fish-oil paints dried much slower than the first series of paints, which were made up with the linseed oil, the No. 3 sample paint being the last of the second series to dry.

(5) A third series of paints were now made up according to the following formulas, standard paints being also made up for comparison (pure spirits of turpentine):

	Parts by weight.
White lead (dry)	40
Sublimed white lead (dry)	60
Zinc oxide (dry)	70
Asbestine (dry)	20
Barytes (dry)	10
Linseed oil	32
Toch drier	0.3
Test turpentine	50

	Parts by weight.
White lead (dry)	40
Sublimed white lead (dry)	60
Zinc oxide (dry)	70
Asbestine (dry)	20
Barytes (dry)	10
Linseed oil	50
Toch drier	0.3
Test turpentine	32

The paints made up according to the first formula dried very rapidly and quite flat. This was due to the large amount of thinners used. The first coat dried hard in one and one-half hours, and there was no appreciable difference in the drying time of any of the paints. The test turpentine paints and the standard paints were applied to steel plates and were exposed to the weather October 16, 1911, and examined July 28, 1912. It should be noted that the paints mixed according to the above two formulas were applied over two priming coats of red-lead paint.

(6) Examination of the paints showed the paint surface to be still intact but easily chalked up, though no signs of corrosion were apparent. The test turpentine paints were equal in all respects to the pure spirits of turpentine paints.

(7) The paints made up according to the second formula were applied, as in all cases, for exposure test against standard paints on steel plates, and these paints were exposed to the weather October 16, 1911. The drying of these paints was somewhat slower than the first formula paints of the third series, but not excessively, the first coats drying in three hours. The paints containing samples Nos. 2, 4, and 5 were somewhat more rapid than No. 3 paint. The results of the examination showed the paints to be in very good condition, chalking but slightly and protecting well the steel plates.

(8) A series of inside white paints were made with the test turpentines, compared to standard inside white paints containing pure spirits of turpentine. The following formula was used:

	Parts by weight.		Parts by weight.
"Ponolith"	60	Linseed oil	50
Zinc oxide	120	Manganese drier	2
China clay	20	Test turpentine	50

The inside white paints, made up according to the above formula, were applied in different parts of a large room at separate times, so that the effect of painting in a confined space might be determined; no ill experience by the painters, and the odors were not unpleasant.

(9) The chemical analysis of the various samples of wood turpentine submitted follows. The samples show on examination:

	Sample.			
	2	3	4	5
Flash (open tester)° F.	104	112	104	104
Specific gravity at 60° F.	0.8670	0.8614	0.8680	0.8644
Refractive index at 60° F.	1.4703	1.4768	1.4718	1.4704
Residue on evaporation at 212° F. per cent.	2.90	1.66	1.38	1.62
Unpolymerized residue, sulphuric-acid test, after ¾ hour standing inches.	2.5	1.7	2.5	3.3
Unpolymerized residue, after 1 hour standing inches.	4.2	3.3	4.2	5.0
Color	Yellowish.	Greenish yellow.	Water white.	Yellowish.

None of the samples leave a spot when one drop is evaporated from filter papers.

When subjected to distillation, 86 per cent of sample No. 2 passes over between 309° and 330° F., 96 per cent having passed over when a temperature of 355° F. has been reached; 55 per cent of sample No. 3 passes over between 314° F. and 330° F., 96 per cent having passed over when a temperature of 362° F. has been reached; 91 per cent of sample No. 4 passes over between 309° F. and 330° F., 97 per cent having passed over when a temperature of 350° F. has been reached; 89 per cent of sample No. 5 passes over between 311° F. and 330° F., 97 per cent having passed over when a temperature of 350° F. has been reached.

All possess the characteristic odor of wood turpentine.

It will be noted from the above chemical analysis that the samples are not in conformity with the specifications for spirits of turpentine, 52–T–2, of December 30, 1911, in the distillation tests; all practically conform in specific gravity;

all conform to the sulphuric-acid tests and further conform to the refractive index test. Sample No. 4 is the only sample reported as "water white."

(10) In summing up the results obtained on the various tests to which the four samples of wood turpentine were subjected it is considered that they have proved to be entirely satisfactory for use in paints (both inside and outside paint) and that they are good grades of wood turpentine.

R. STOCKER.

[1st indorsement.]

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